THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

CORROSIVITY OF KRAFT LIQUORS

PHASES II AND III

Project 2926-6

Report Two

A Progress Report

to

FOURDRINIER KRAFT BOARD GROUP

OF THE

AMERICAN PAPER INSTITUTE

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PHASES II AND III

SUMMARY

This report describes the progress of FKBG project activities since the previous publication in 1979. The details in planning and constructing a hot corrosion laboratory are given. Corrosion test results on mild steel, Type 304 stainless steel, and weldments of these metals are described. The appropriate test environments were weak and heavy black liquor and white (clarifier) liquor. A literature review of recent reports on the corrosivity of kraft liquor and related environments is included; it covers the literature since the previous review by this agency in 1979 (see "Corrosivity of Kraft Liquor," IPC Project 2926-56, A Progress Report). The need for future corrosion studies in linerboard pulp mill environments is discussed in the final section of the report.

INTRODUCTION

In mid-1978, The Institute of Paper Chemistry embarked on a program to study the corrosivity of kraft liquors. The applied research part of this program was sponsored by the Fourdrinier Kraft Board Group (FKBG) of the American Paper Institute. Phase I of the FKBG project consisted of the determination of serious pulp mill corrosion problems in the linerboard industry. This objective was accomplished by mill survey and visitation; the results were published in 1979 (see Progress Report One, "Corrosivity of Kraft Liquors," A Progress Report to FKBG, January 15, 1979). The purpose of this report is to provide an update of progress on the subsequent phases of this study (1979-1981). In addition, at the request of the FKBG Technical Committee and Board of Directors, this report also includes a review of recent literature as it pertains to the general subject of corrosion by kraft liquor(s). Therefore, this report is comprised of three major parts. The first section(s) reports the progress of the FKBG project since the completion of Phase I. A literature review is provided in the second section. The third part deals with future plans and how this proposed work fits in with past and current research by this agency as well as others.

Phase II of the FKBG program was aimed at the assessment of corrosivity in the previously identified problem segments of the kraft cycle, namely, low solids, weak liquor; white (clarifier) liquor; and high solids, heavy black liquor. It was necessary to build a laboratory capability to conduct this program. In the following sections of this report, the hot corrosion lab facility is described, since its construction was a major part of the Phase II program. The laboratory is comprised primarily of three all-Teflon constructed test systems which allow for the circulation of sufficient liquor corrodent to measure metallic corrosion processes by weight loss and/or electrochemical techniques. In addition to liquor studies, these

systems were built to provide for future testing with more harsh chemicals, e.g., bleach solutions, tall oil, acidulated liquors, caustic or acid makeup additives. The equipment and instrumentation for hot corrosion testing are also described in the following sections.

The major forms of corrosion investigated in the subsequent test programs were concentration cell and uniform attack in weak liquor, uniform and erosion-corrosion (with and without galvanic acceleration) in white clarifier liquor, and uniform corrosion in heavy black liquors. FKBG member company mills supplied the test liquors for this investigation. The test materials were mild steel, Type 304 and 316 (selected tests only), stainless steel, and weldments of these metals.

One major finding in subsequent corrosion tests was that problem liquors at the mill were not corrosive in the laboratory. The corrosivity of white liquor (the most corrosive medium) seemed to be related to thiosulfate concentrations; however, liquor analyses, i.e., analytical techniques, became questionable. About this same time, other researchers reported corrosion studies in white liquor. Their work confirmed the need to continue pursuit of white liquor corrosivity studies, but the original scope of this aspect of our program required modification. Weak liquor corrosivity toward mild steel was greater for higher solids brown stock washing filtrates, i.e., corrosivity of first stage > subsequent stages. The metal damage was primarily associated with corrosion product/liquor solids attachment at random, local sites. Heavy black liquor corrosivity was related to a combination of solids and condensate from those systems. Further details of Phase II results and the work of others is reported in the following sections.

Phase II research expectations were frustrated due to time delays in equipment delivery that caused complications in lab construction and complexities in

corrosivity measurements, i.e., sampling, testing, and analyses. However, there were worthwhile results on kraft liquor corrosivity as a function of temperature, aeration, and solids content and chemistry, as described later. Furthermore, lab equipment requirements, techniques, and practice for "safely" studying corrosion in hot, kraft liquors were established. These findings, together with careful reviews by this agency and sponsor, set the stage for Phase III.

During 1981, preparations were made to continue the pursuit of causative factors in the corrosion of mild steel in weak, heavy black, and white, clarifier liquors, i.e., Phase II liquor systems. Among the unknown factors responsible for accelerated corrosion, the effect of stress was considered as a causative agent. Preliminary tests in weak liquor at low levels of stress (1000 to 3000 psi) showed little change in mild steel's corrosion rate unless liquor chemistry was changed. The stress cells were modified to accommodate higher applied stresses. In addition to stress tests, applied potential techniques called "zap" tests were developed which allowed better assessments of weak liquor corrosivity. This made it possible to stimulate significant and reproducible corrosion on mild steel in weak liquor (in some cases even stainless steel) which was not possible in Phase II. Finally during the Phase III, 1981 program, preparations were made to implement a simultaneous in-mill and laboratory test program planned for 1982. The final section of this report describes those plans for 1982 as these relate to past IPC/FKBG kraft liquor studies and similar studies by others.

PHASE II - FKBG/IPC PROJECT 2926-6 (1979)

Corrosion Research Facility

To meet the requirements for lab space to perform corrosion tests in kraft liquors as well as that for current and future projects, the annex building at the

Institute was provided as the site for future research. The location of this building is shown in Fig. 1. Several research projects, both Institute and government sponsored, have been conducted there in the past. As some of these projects were closed, the building was used as a storage area. We began renovation of this building in the late fall of 1978.

Figures 2 and 3 show the floor plan layouts of that portion of the annex undergoing current conversion to corrosion laboratories. The first floor plan (Fig. 2) shows the areas designated for staff offices, chemical makeup, aqueous, and hot corrosion labs. The hot corrosion lab provides lab bench space to install three cells for circulating hot liquor, electrochemical instrumentation, timers, and recorders. Corrosion studies of mild steel and stainless steel in white liquor clarifier slurries, weak filtrate, and heavy black liquors were performed at this location. This room also accommodates the cold storage cabinet necessary for environmental preservations in this and other projects.

The layout of the second floor (Fig. 3) shows the area designated for erosion-corrosion equipment and proposed sites for stress corrosion and coatings/nonmetallics testing laboratories. Although these applied research studies were frequently proposed from 1979 to the present, approval is still pending. Staff offices, as well as equipment assembly areas, are also shown on this floor. At this time, at least, these sites have been cleared of storage and prepared for future studies. Top priority was directed toward the completion of the hot corrosion lab, which will contain a closed circulating liquor system and a pressurized piping/storage system to support the proposed work of this project.

Description of Laboratory Equipment

Electrochemical studies of kraft liquors require systems free of contamination, moderate temperatures, and continuous flow. For this purpose, three all

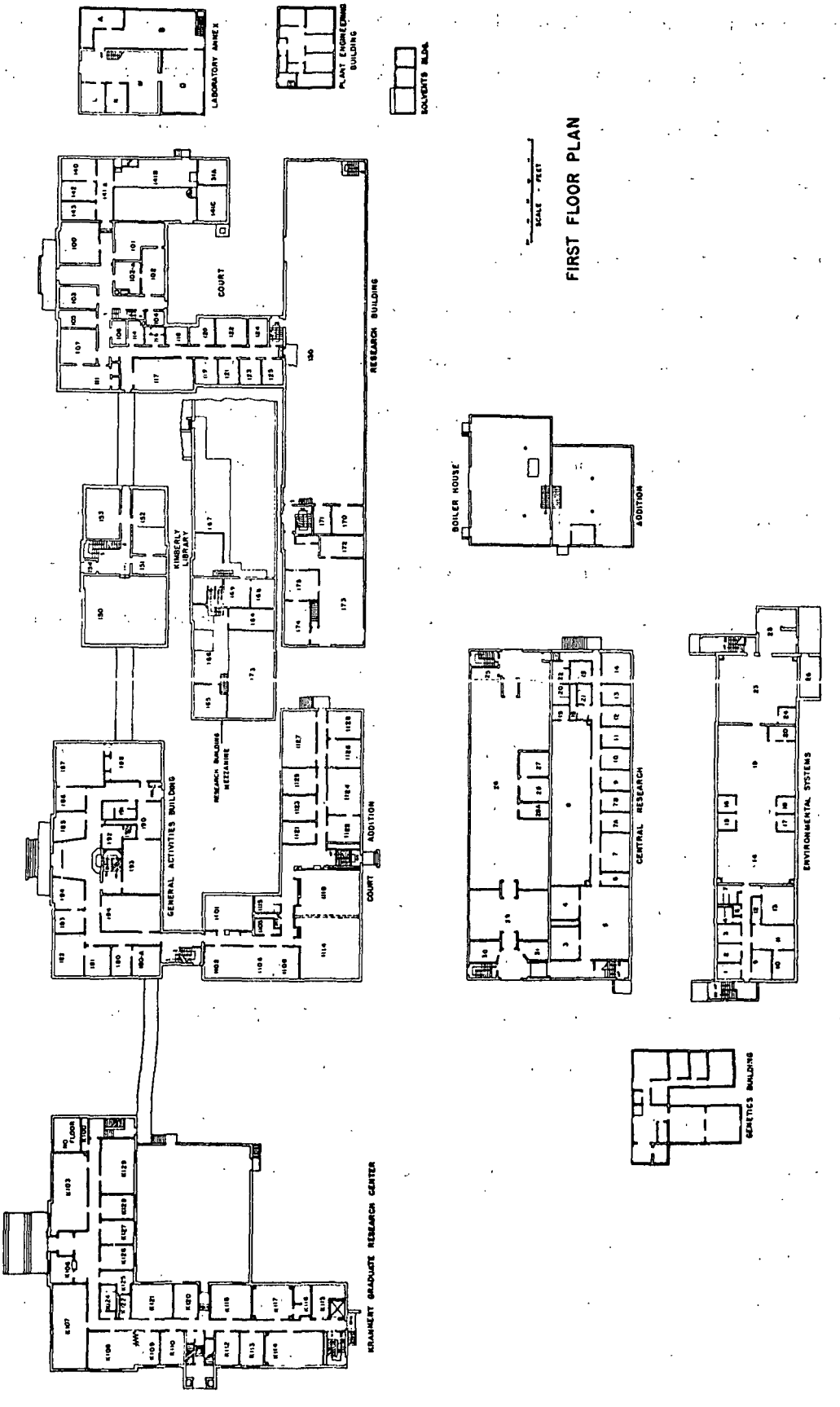

Figure 1. Map of IPC facilities - first floor plan - showing the location of corrosion research laboratories in Laboratory Annex Building (upper right).

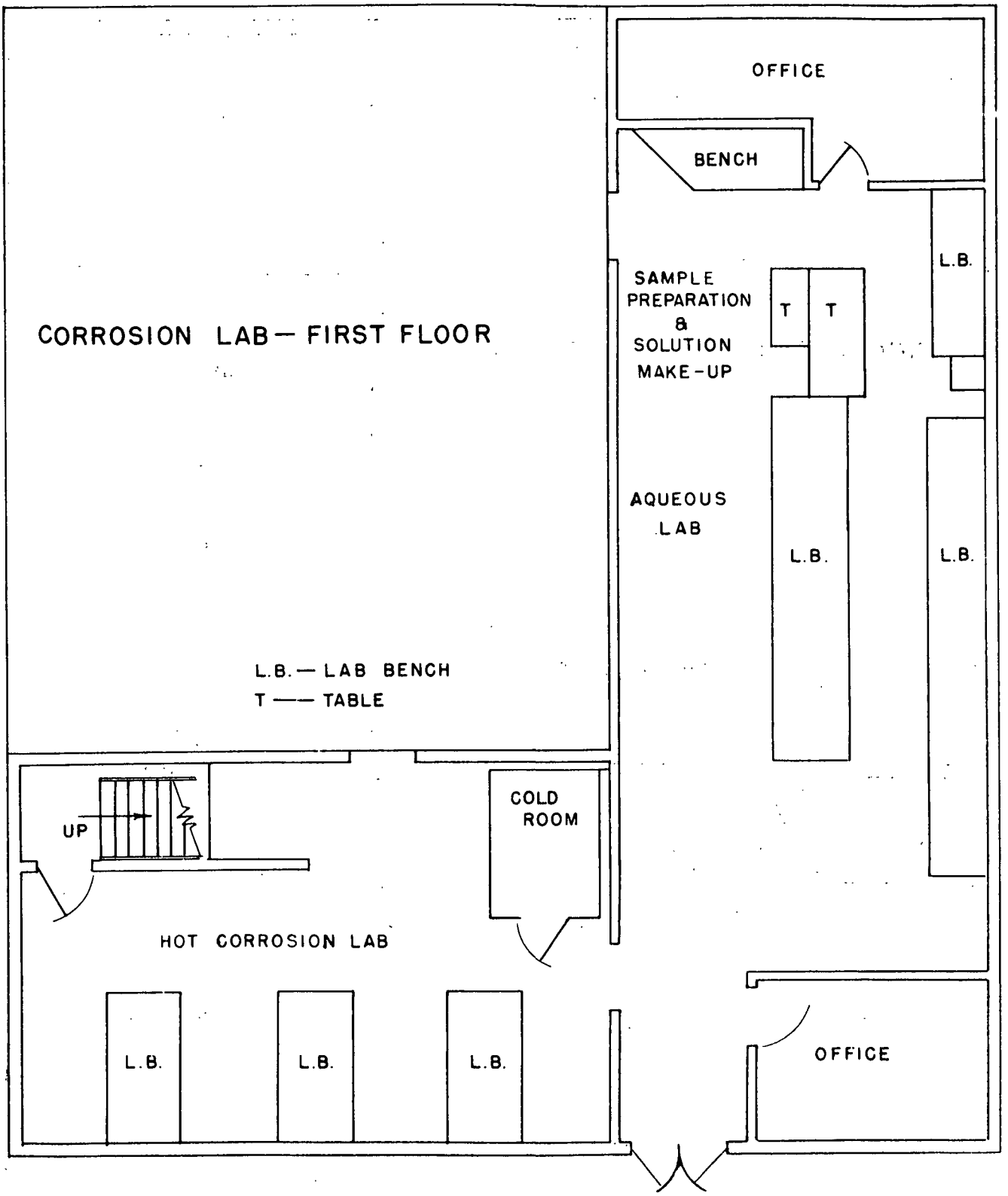

Figure 2. Layout of first floor plant of Annex Building showing the location of aqueous and hot corrosion lab facilities.

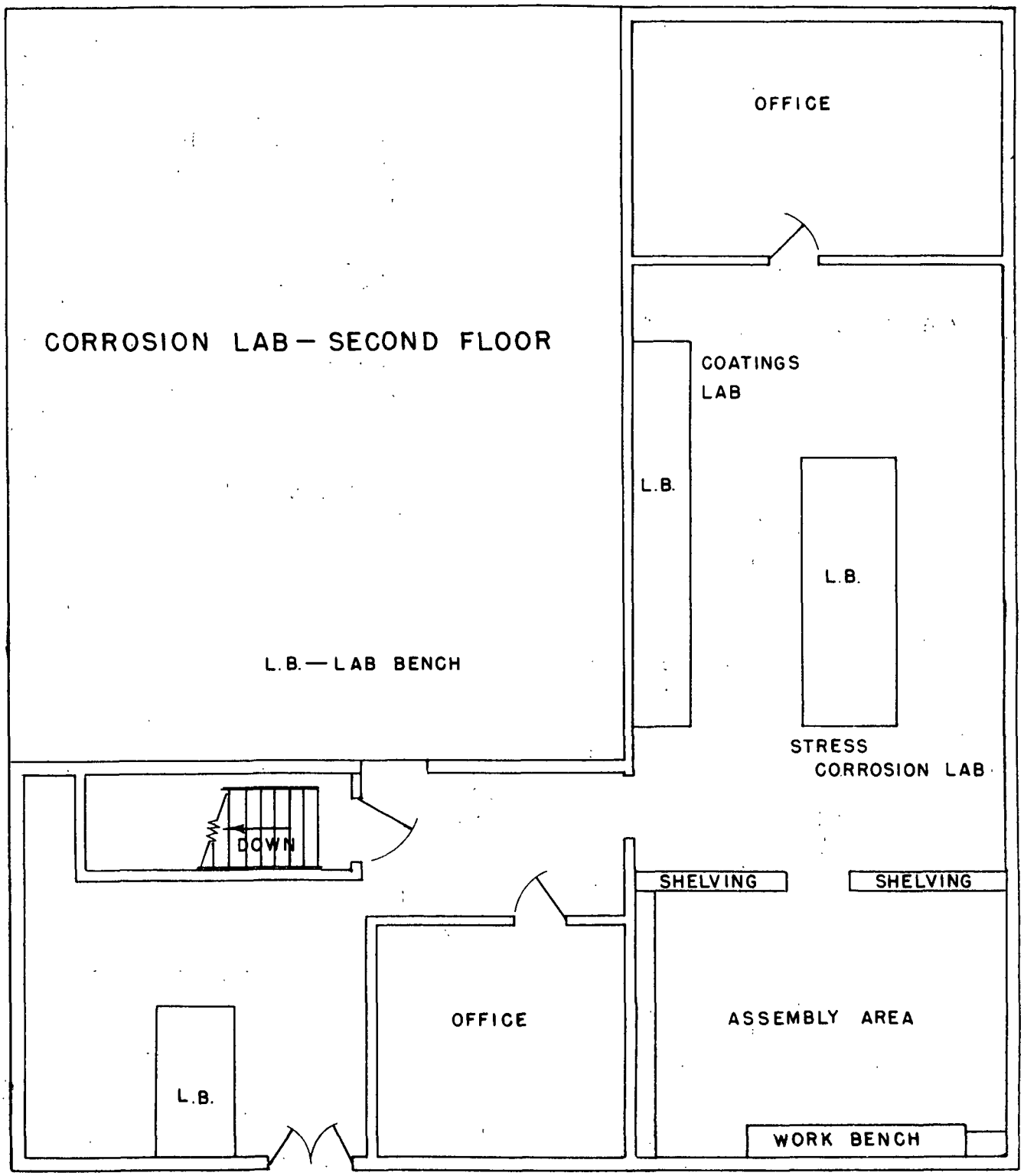

Figure 3. Layout of second floor plan of Annex Building showing locations for erosion corrosion, stress corrosion, and coatings/nonmetallics labs.

Teflon/Kynar constructed test systems were assembled, and on-line electrochemical instrumentation was installed. Figure 4 shows the basic components for this test system; it is comprised of a 2-gallon Teflon container, a 45 watts/ft (Teflon) heating coil, and a 1/4-horsepower, circulating (Teflon) pump (12 gal/min, maximum); flow direction is from the side (at top) to a drain hole in the bottom. All plumbing is Kynar construction.

Figure 5 is a view of the test system assembled. This system was initially used to simulate a white liquor clarifier. A close-up view of the top, showing the motor/belt drive, rotating mercury contact, and electrode holders is seen in Fig. 6. The system incorporates rakelike coupons for weight-loss measurements and a rotating electrode for electrochemical studies. These test specimens are shown in Fig. 7. To position the reference electrode in close proximity to the rotating (working) electrode, the electrode holder was put through a compression fitting on the rear of the autoclave. This is shown in Fig. 8.

Figure 9 shows the corrosion test system and instrumentation for the weak liquor studies. A close-up view showing the positioning of the electrodes required for these studies is shown in Fig. 10 and 11. The system is used for deposit corrosion studies and polarization/weight-loss testing.

A third test system for heavy black liquor corrosion tests was constructed. This simulation required that test specimens receive alternate exposure to vapor/

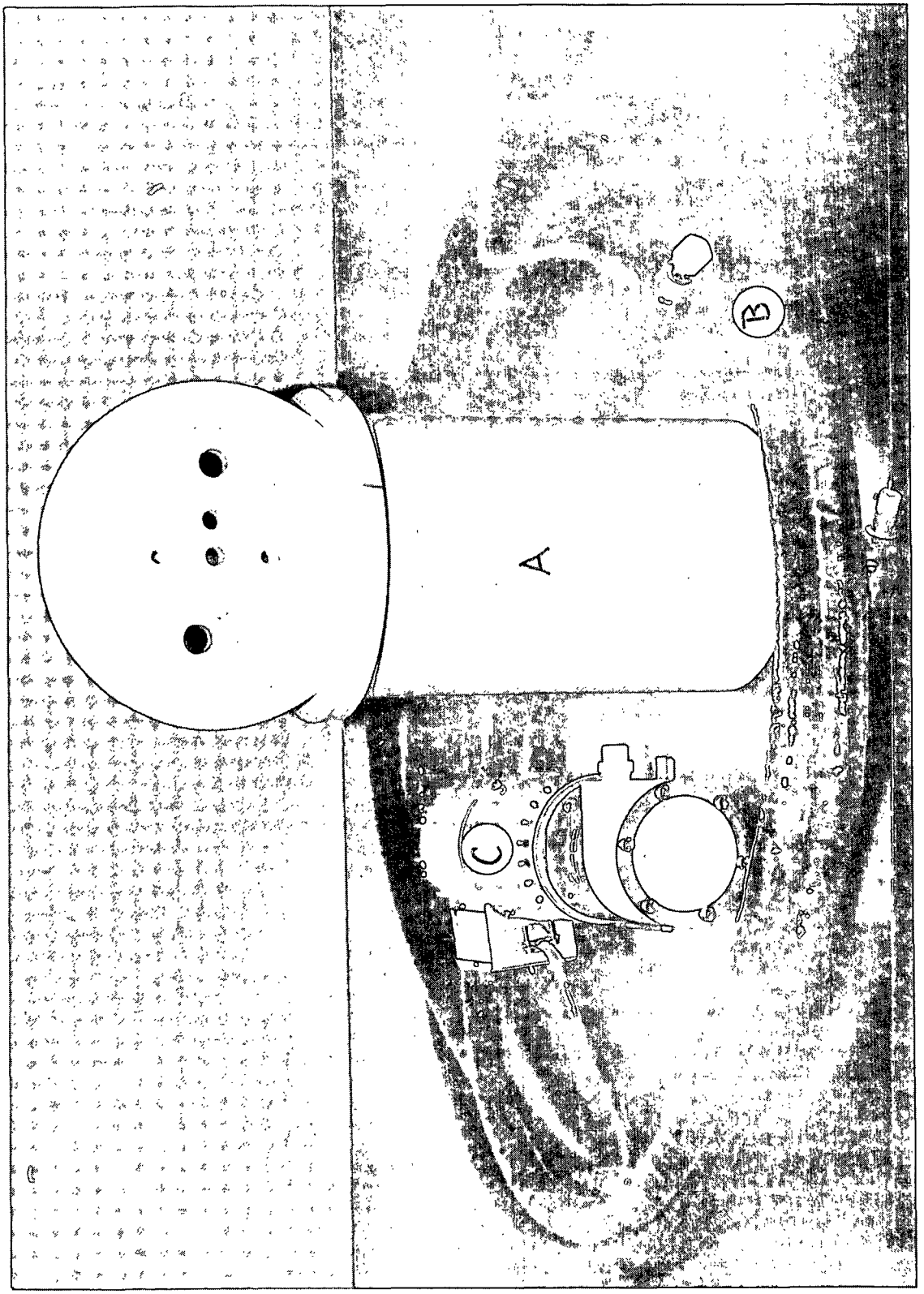

Figure 4. Photograph showing basic components of the test systems -

A Container (corrosion test cell)
B Teflon heating coil
C Circulating pump

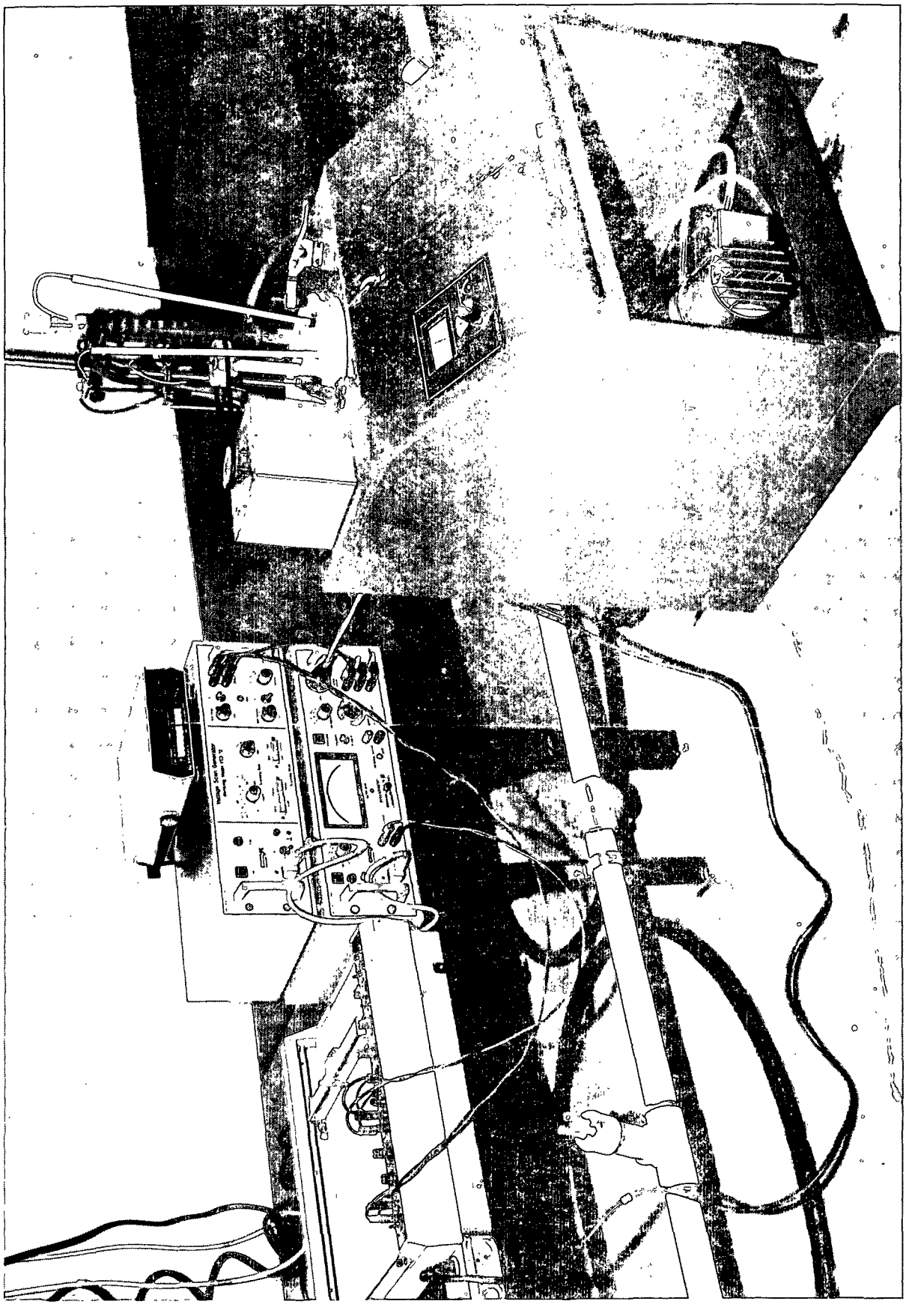

Figure 5. Photograph showing the test systems to simulate a white liquor clarifier. Instrumentation to monitor electrochemical behavior of rotating electrodes is shown in the background.

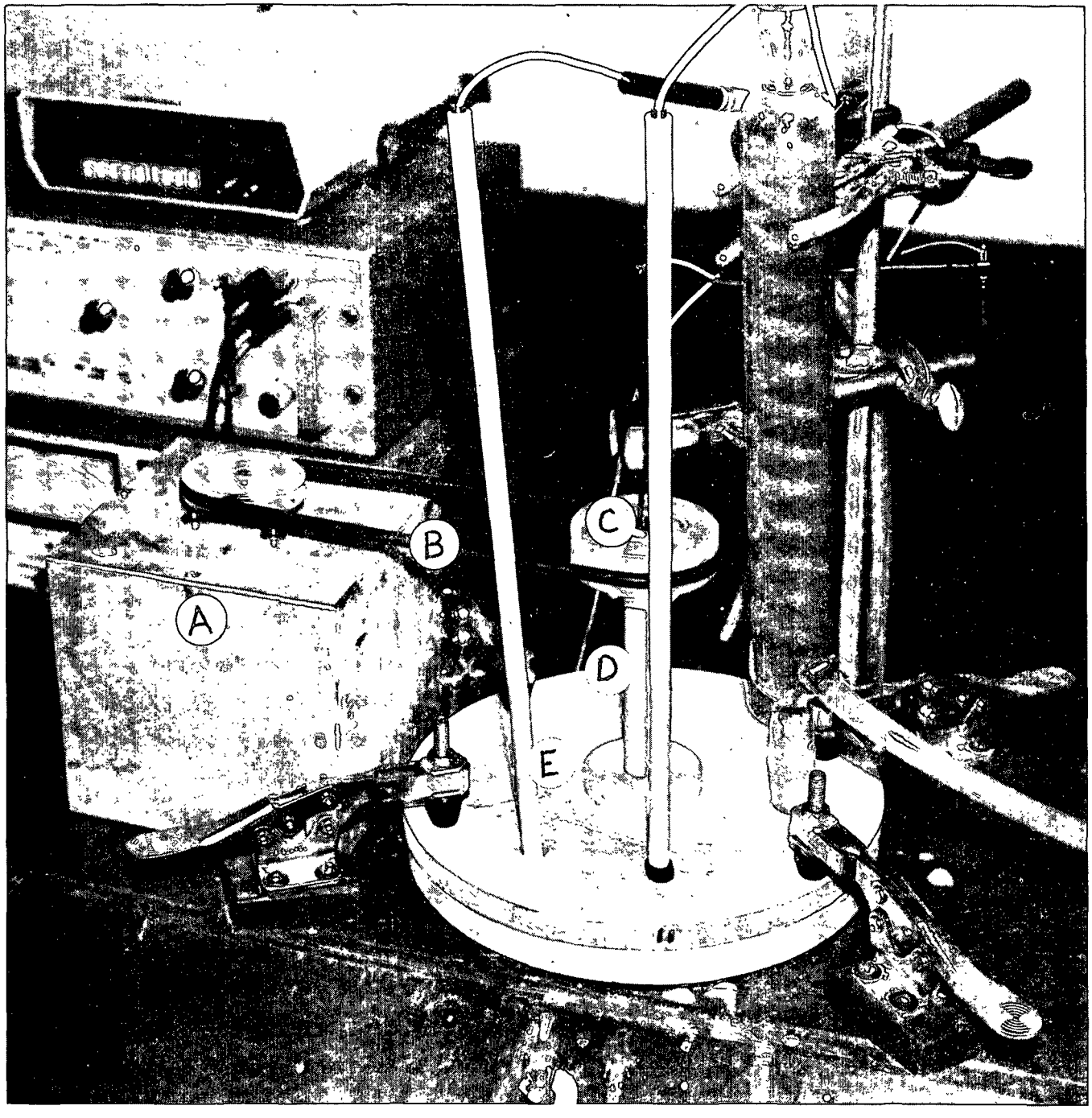

Figure 6. Close-up view of the top of the white liquor clarifier-simulator

A Drive motor and pulley
B Belt
C Mercury contact for rotating electrode
D Teflon shaft
E Counter electrode holders

condensate and liquor phases similar to heavy black liquor storage tanks. A time-programmed valve network and storage reservoir allow changes in liquor level so that appropriately positioned test specimens simulate the required exposure conditions. Figure 12 shows the time programmer we constructed for this purpose. Time sequences in this programmer can vary from seconds to 60 hours.

Figure 7. View of rakes (A) and rotating electrode (B) attached to Teflon shaft.

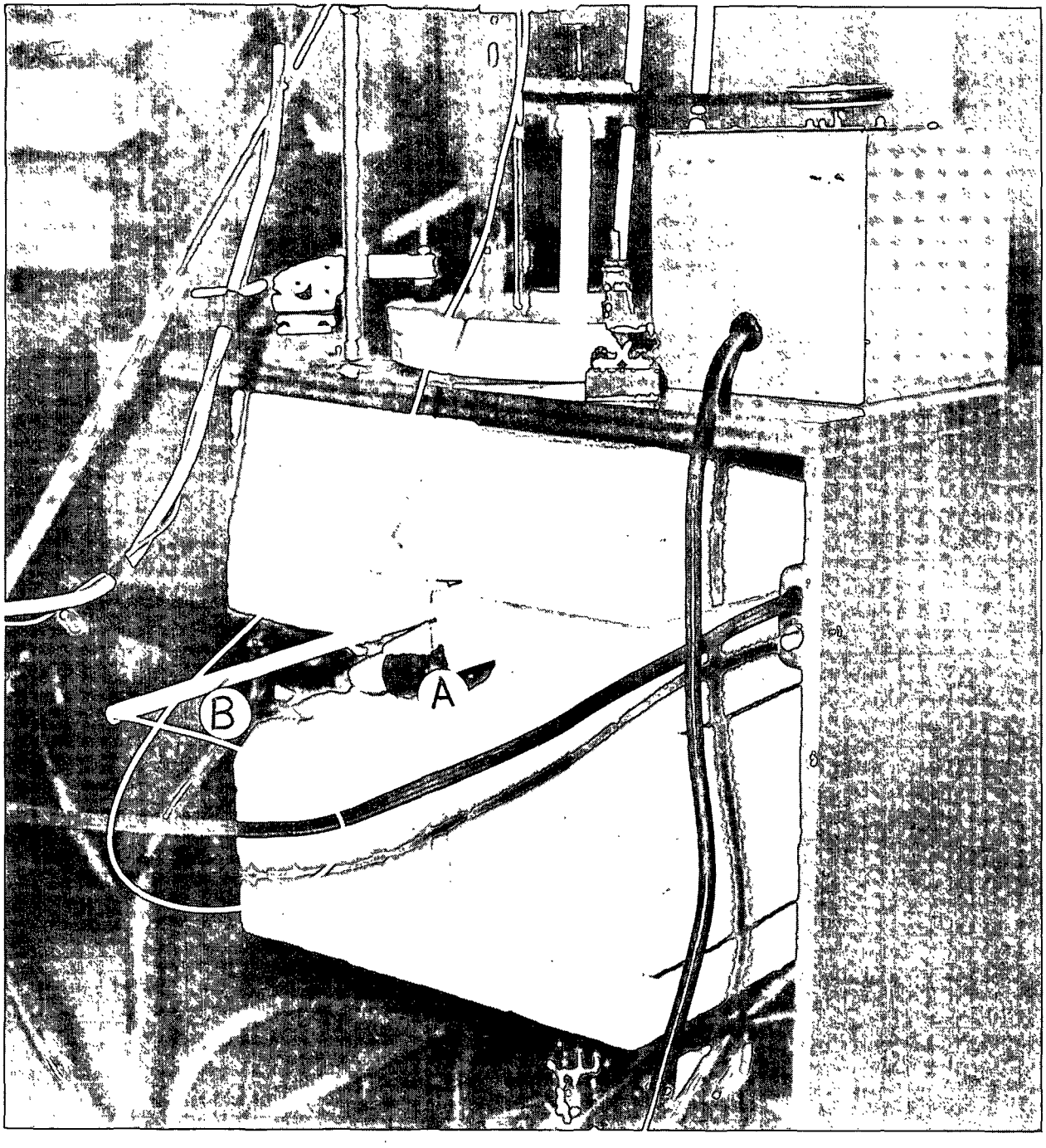

Figure 8. View of the back of the white liquor clarifier-simulator showing the insulation, location of liquor inlet (A) and the position of the reference electrode holder (B).

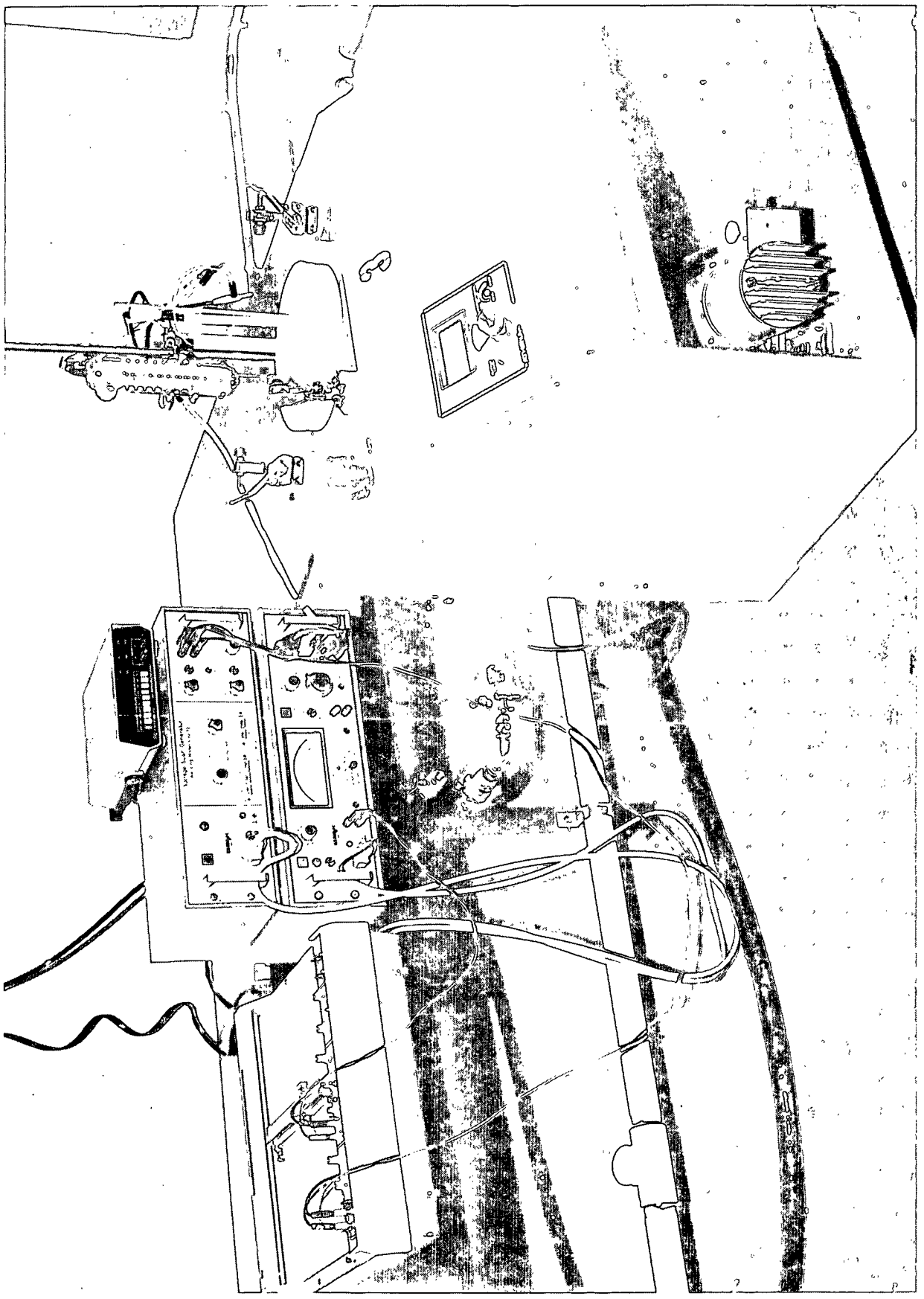

Figure 9. A view of the test cell and instrumentation (in the background) which is being used to study weak liquor corrosivity and deposit corrosion.

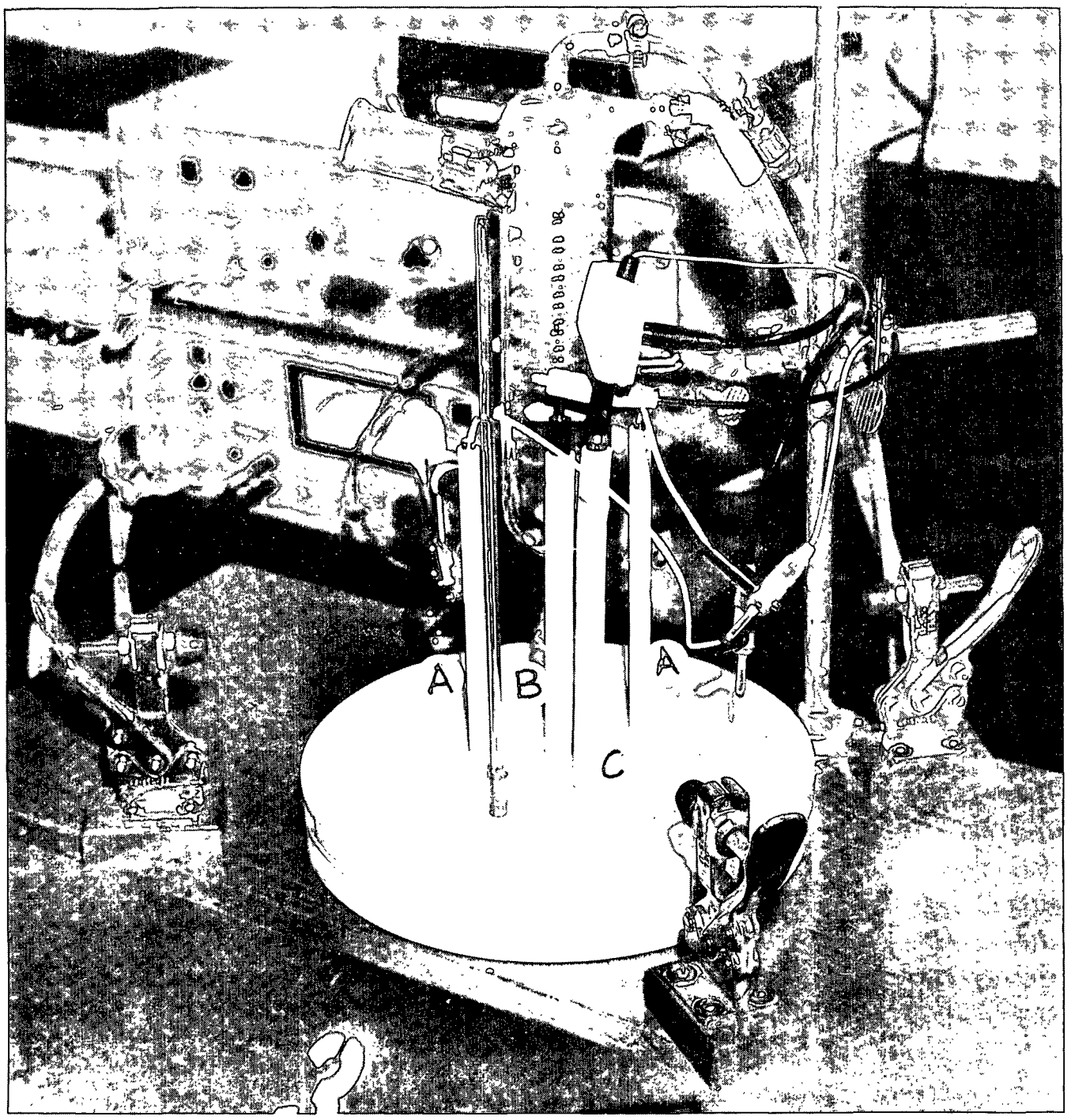

Figure 10. Close-up view of the top of the weak liquor test cell showing the position of the electrodes as follows:

A Counter electrode holders
B Working electrode holder
C Reference electrode holder

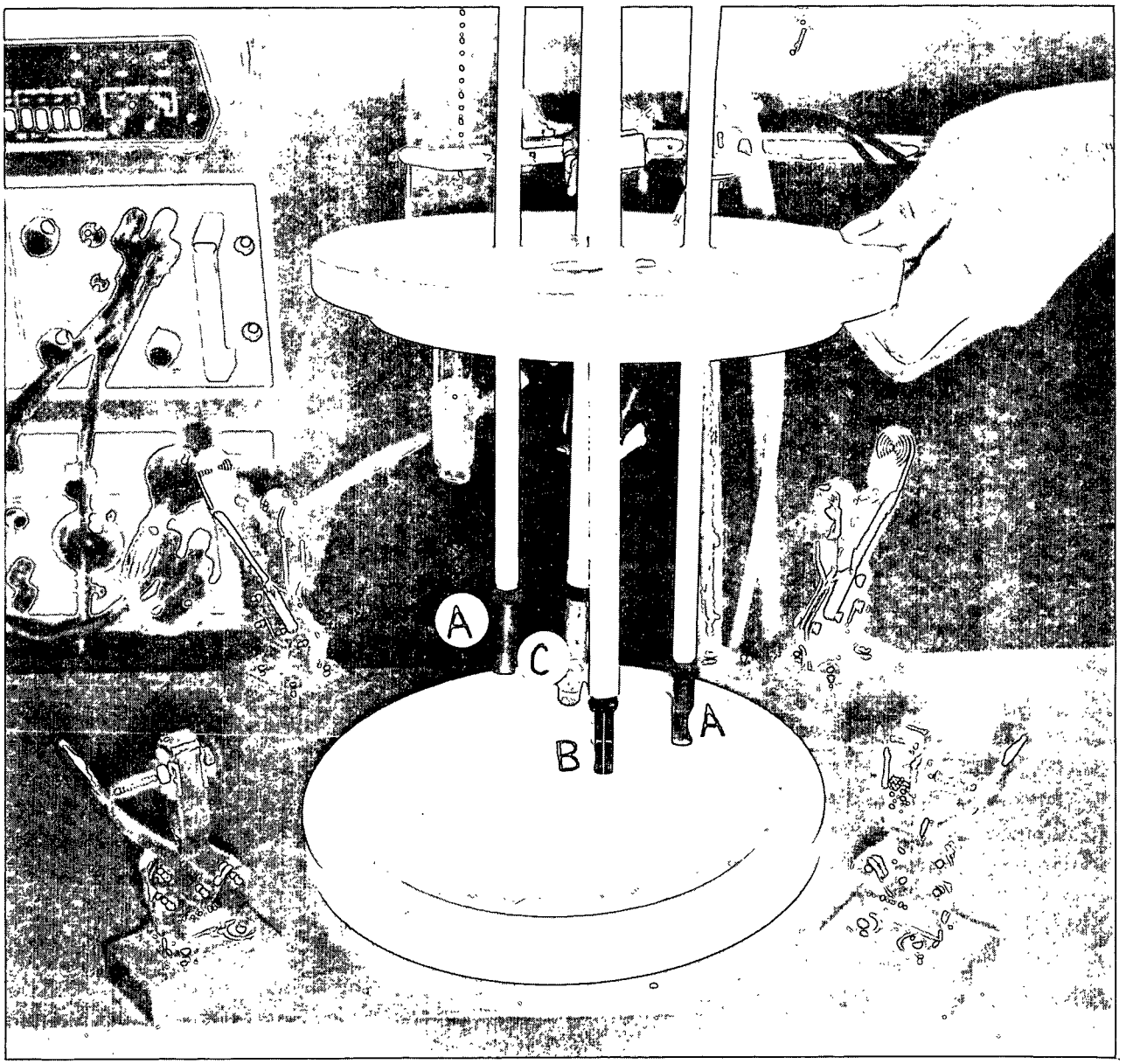

Figure 11. View of the electrodes used for electrochemical tests in kraft liquor

A Graphite counter electrodes
B Mild steel working electrode
C Lazaran (Ag-AgCl) reference electrode

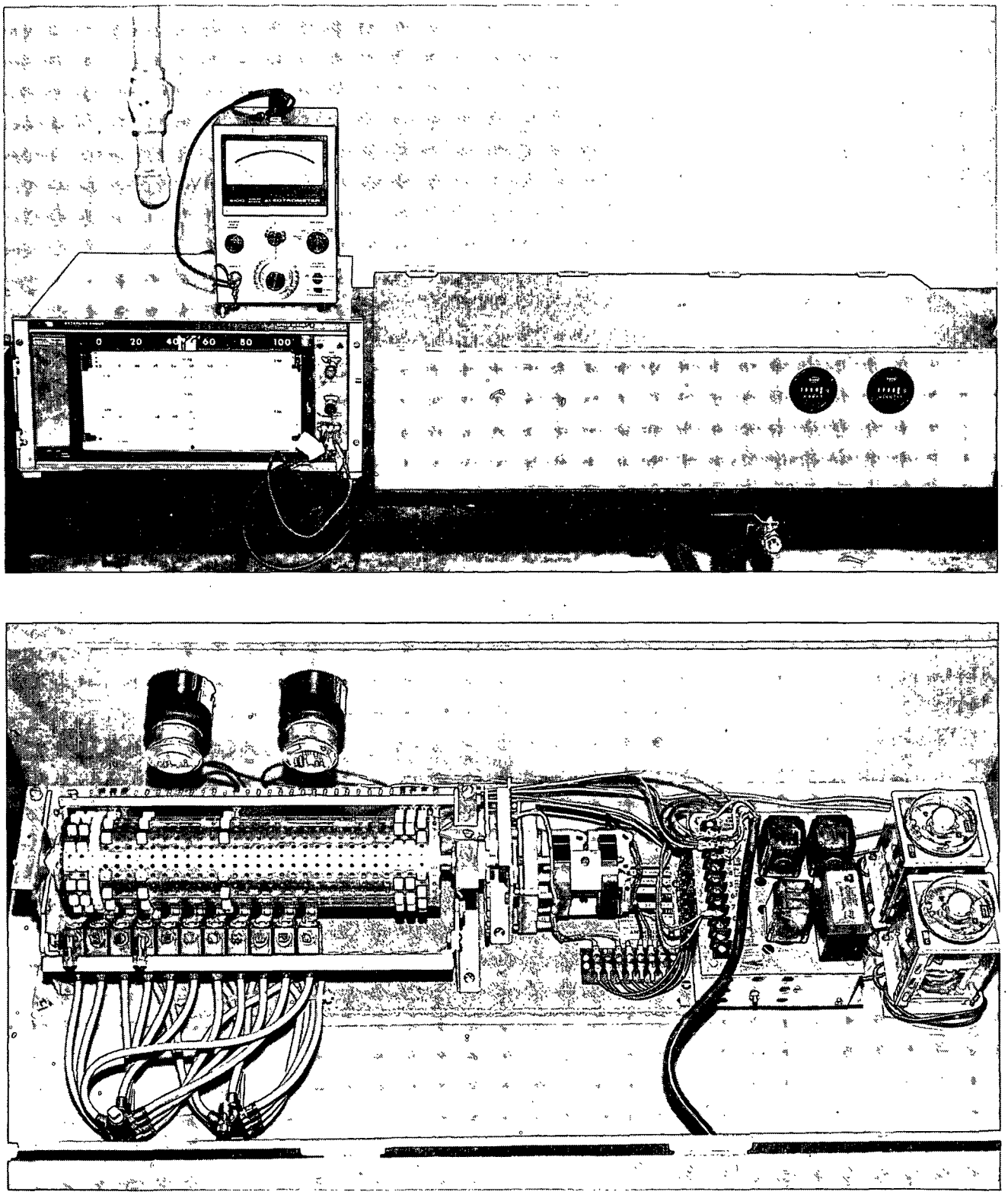

Figure 12. View of programmer to change liquor levels in number 1 test system for heavy black liquor. Top photo-programmer enclosed in cabinet, time meters at (A). Bottom photo, view of programmer mounted inside of cabinet.

Test Materials and Procedures

The chemical composition of all test materials used in the corrosion tests described in this report are shown in Table I. Information describing the welding process, filler metal, etc., for weldment tests is also indicated. The bulk of testing in weak liquor was performed using plate material, whereas tests in white liquor employed rod or cylindrical electrodes.

TABLE I

CHEMICAL COMPOSITION OF TEST MATERIALS

Alloy	Content (wt. %)							
	C	Mn	Si	P	S	Ni	Cr	Mo
Type 304 stainless	0.065	1.46	0.32	0.024	0.023	8.68	18.90	--
Type 316 stainless	0.056	1.40	0.50	0.031	--	13.10	16.90	2.15
Mild steel (plate)	0.23	0.76	0.05	0.006	0.020	--	--	--
Mild steel (rod)	0.23	0.40	0.01	0.005	0.034	--	--	--
Mild steel (weld)	0.17	0.78	0.18	0.004	0.019	--	--	--

Welding Procedures

	Process	Filler Metal
Mild steel	Manual	E6010
304	Automatic (MIG & TIG)	304

Electrochemical polarization tests were conducted at a scan rate of 0.6 volt per hour using graphite counter electrodes and Lazaran reference electrodes. Crevice corrosion tests were performed by clamping a deposit on the surface of the plate and measuring the applied potential necessary to activate corrosion beneath the deposit. A scan rate of 0.024 volt per hour was used in these tests. Potential

decay tests were made by measuring the working electrode potential (electrical voltage at the surface in a "freely" corroding state) with respect to the Lazaran reference electrode as a function of time. A Keithley electrometer and linear recorder served as instrumentation for decay measurements.

Corrosion Testing - Preliminary Results White Liquor (1980)

This test program was directed toward the establishment of the technique and equipment necessary for clarifier simulation. The test system employed rotating rakes and electrodes. Tests were also conducted on stationary electrodes for comparison. It was also important to study the electrochemical behavior of stainless steel compared with mild steel in white liquor and the differences in this behavior as a function of liquor sampling location and storage time prior to testing. To study these effects, white liquors were obtained from a local mill.

Figure 13 shows the potential decay behavior of mild steel and Type 304 stainless steel in clarifier white liquor. The data indicate that the stainless steels remain clean and passive throughout the test period. This was verified after testing, since the surface retained its original, bright luster and there was no indication of corrosive attack. The mild steel electrode was heavily encrusted with a black surface deposit. However, the mild steel potential decay data in Fig. 13 do not indicate film formation. Instead, the surface potential remains close to its starting valve throughout the test. This inconsistency is currently under investigation; it appears to be related to the stability of the reference electrode. This problem should be resolved prior to planned tests on clarifier liquors from FKBG member company mills.

Figure 14 shows the polarization behavior of mild steel in white liquor sampled from the clarifier and digester. For purposes of comparison, the following symbols, shown on the curves, are defined.

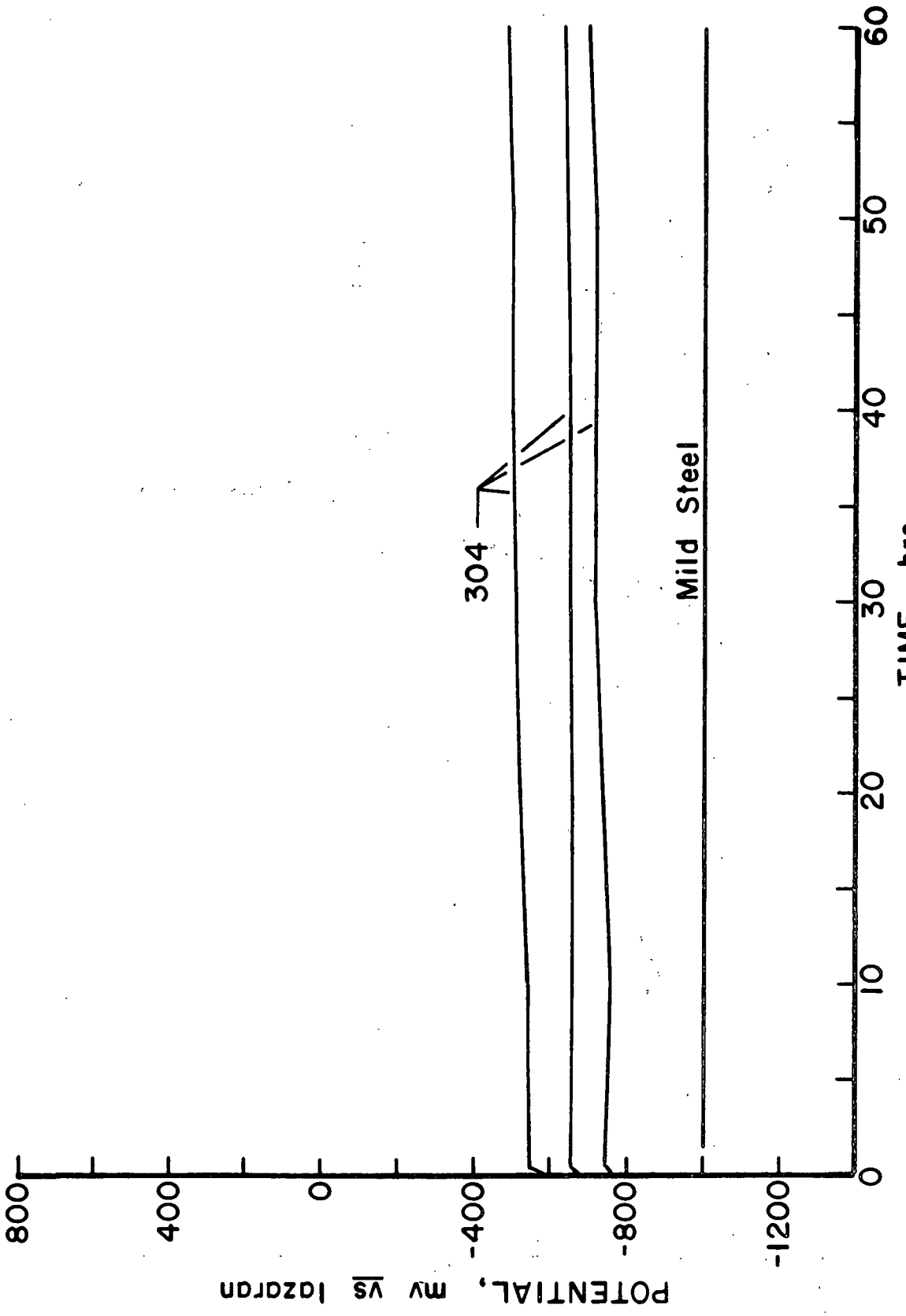

Figure 13. Potential decay of mild steel and 304 stainless steel in clarifier white liquor.

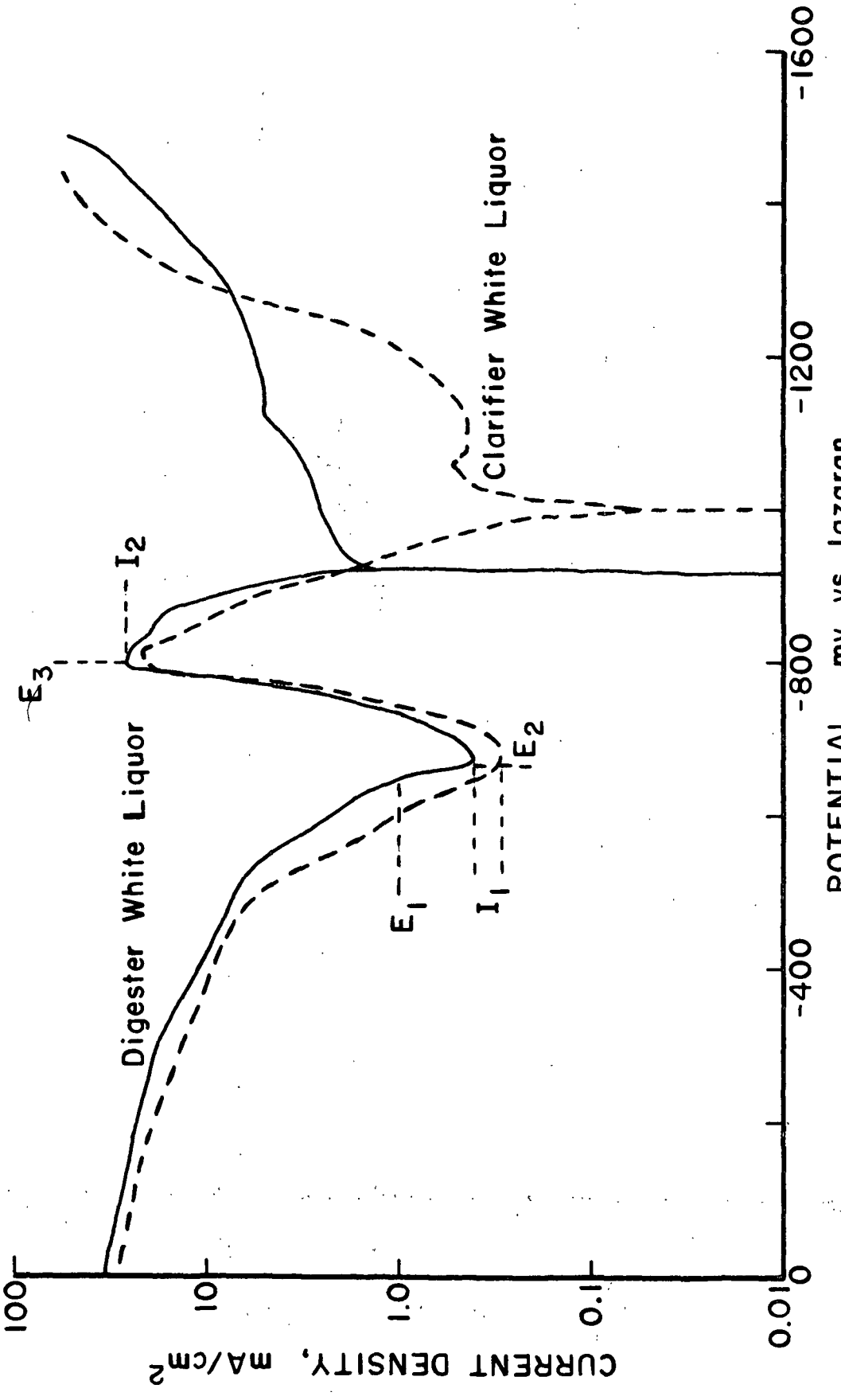

Figure 14. Polarization behavior of mild steel in digester and clarifier white liquor (90°C).

E_1 - An oxidation potential selected at 1 mA/cm^2

E_2 - Potential marking the end of passivity

E_3 - Primary passivation potential

I_1 - Passive current density

I_2 - Primary passive current density

The variation of these values as a function of liquor age (time from sampling to the completion of test) is shown in Table II. In general, these values show that the loss of chemical reactivity or aggressiveness of the liquor toward mild steel corrosion occurs after 14 days. This is shown by the reduction in E_3 and I_2 values which becomes significant at 14 days, indicating that sampling and testing of white liquor should be accomplished within that time frame.

Figure 15 is a typical comparison of the polarization behavior of Type 304 stainless steel to mild steel. Corrosion product film development and transition from active to passive state occurs on mild steel at approximately -700 mv., Laz. The region of active corrosion on mild steel is quite significant, extending from -1000 to -800 mv. The implication is that this liquor is quite corrosive to mild steel. We expect other liquors to behave differently - depending on composition. This point will become clearer as we combine analytical and electrochemical data in the future white liquor test program. Type 304 remained passive throughout the polarization tests, and the curve shown in Fig. 15 is typical of all tests. Its behavior appears to be related to the oxidation kinetics of the liquor and not metallic dissolution.

Figure 16 reflects the change in polarization for mild steel as a function of age. In this case, the general shape of the curves is the same, but a shift to more noble potentials is indicated for the older liquor. The same behavior was

found for stainless steel (Fig. 17), again demonstrating the need to schedule white liquor tests so that the age is the same and less than two weeks old.

TABLE II

ELECTROCHEMICAL POLARIZATION DATA FOR MILD STEEL IN DIGESTER AND CLARIFIER WHITE LIQUOR

Run No.	Age (days)	Passive Range (mv., Laz.)	E_1 (mv., Laz.)	E_2 (mv., Laz.)	E_3 (mv., Laz.)	I_1 (mA/cm^2)	I_2 (mA/cm^2)
			Digester Liquor (90°C)				
1	12	270	-675	-750	-830	0.45	33
2	14	276	-700	-700	-860	1.0	24
3	21	320	-620	-700	-790	0.20	37
4	49	310	-590	-640	-750	0.35	20
5	50	252	-580	-640	-740	0.56	14
			Clarifier Liquor (90°C)				
1	2	310	-500	-700	-800	1.0	44
2	6	305	-460	-740	-860	0.52	35
3	14	250	-460	-480	-630	0.82	30
4	18	335	-410	-240	-400	0.60	--
5	62	245	+170	+70	-40	0.50	18

Tests were conducted to check for any difference in polarization behavior for rotating versus stationary electrodes and the positioning of test electrodes. Figure 18 shows only minor changes in the shape of the curves obtained for rotating and stationary electrodes. Therefore, future tests in clarifier white liquor can be conducted with either type of electrode.

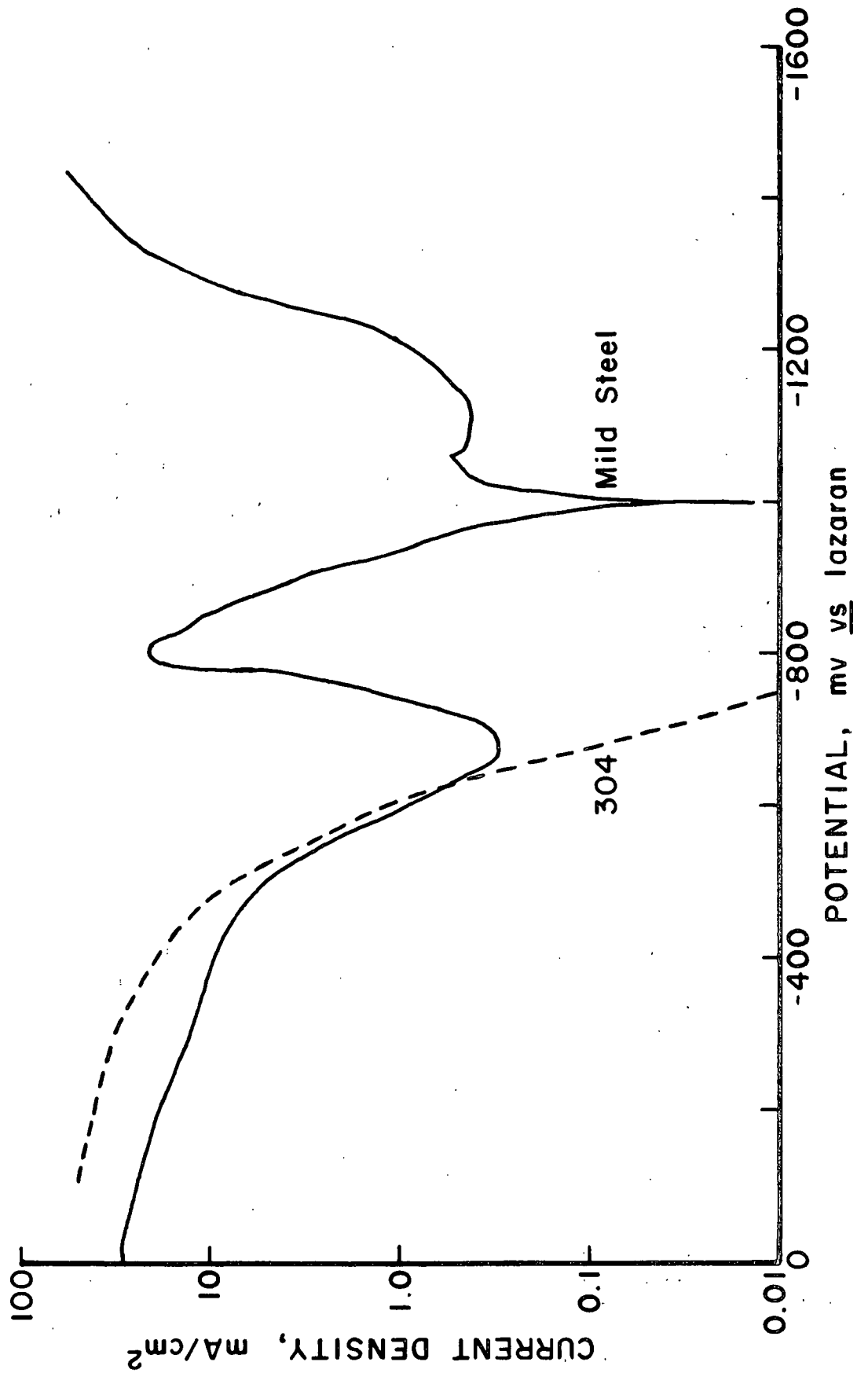

Figure 15. Polarization behavior of mild steel and 304 stainless steel in clarifier white liquor (90°C).

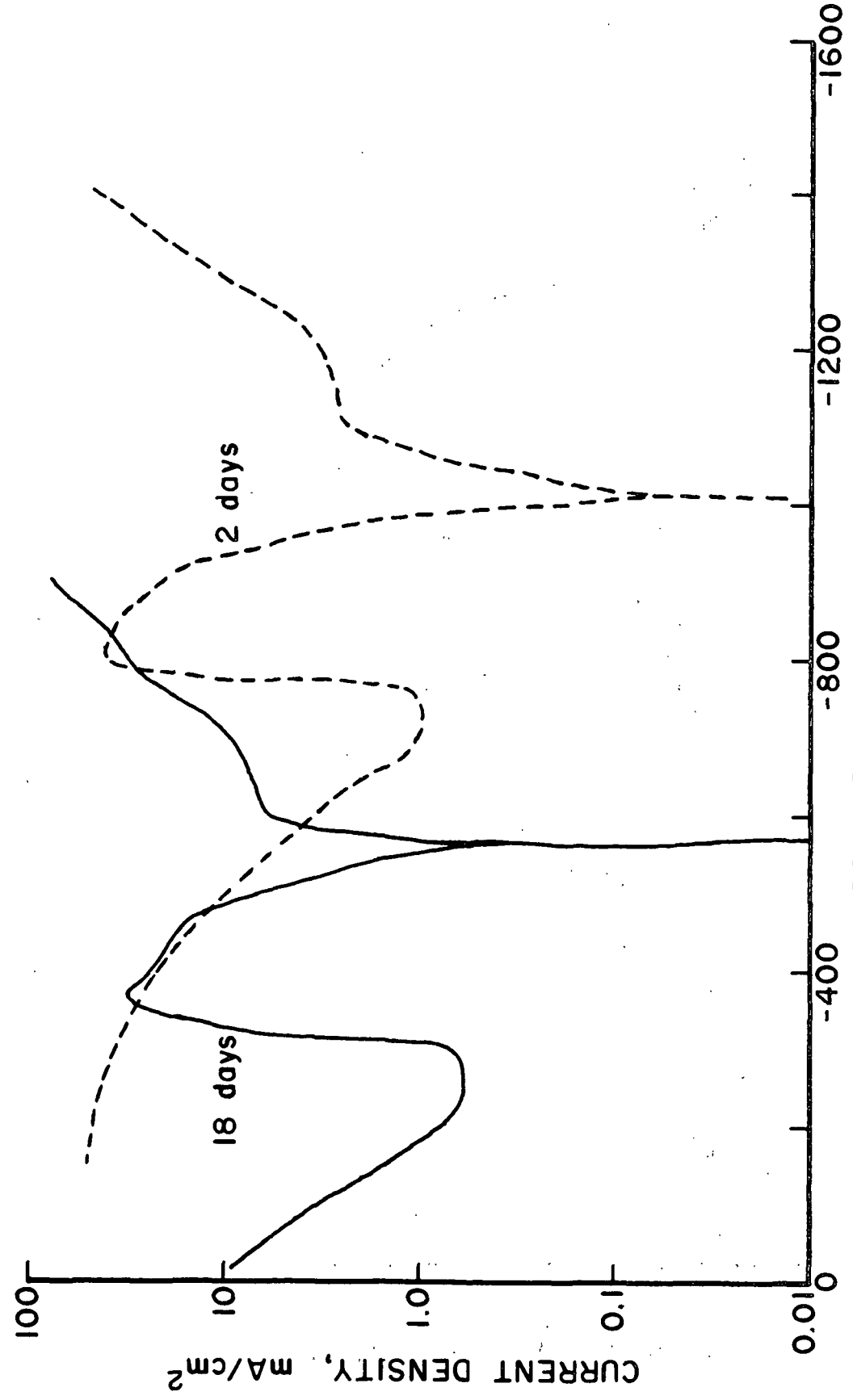

Figure 16. Polarization behavior of mild steel in clarifier white liquor at 2 and 18 days after sampling (90°C).

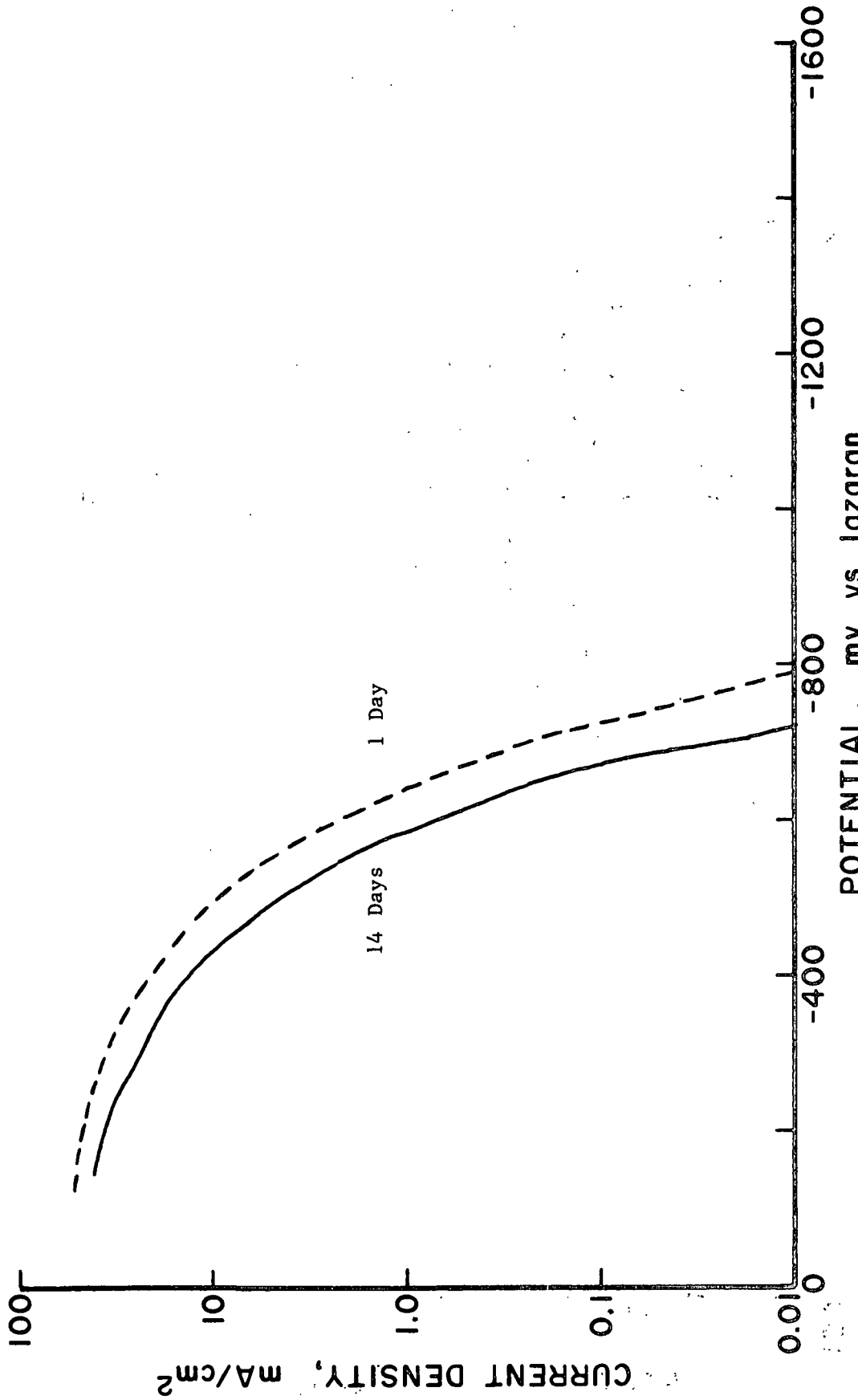

Figure 17. Anodic polarization behavior of 304 stainless steel in clarifier white liquor at 1 and 14 days after sampling (90°C).

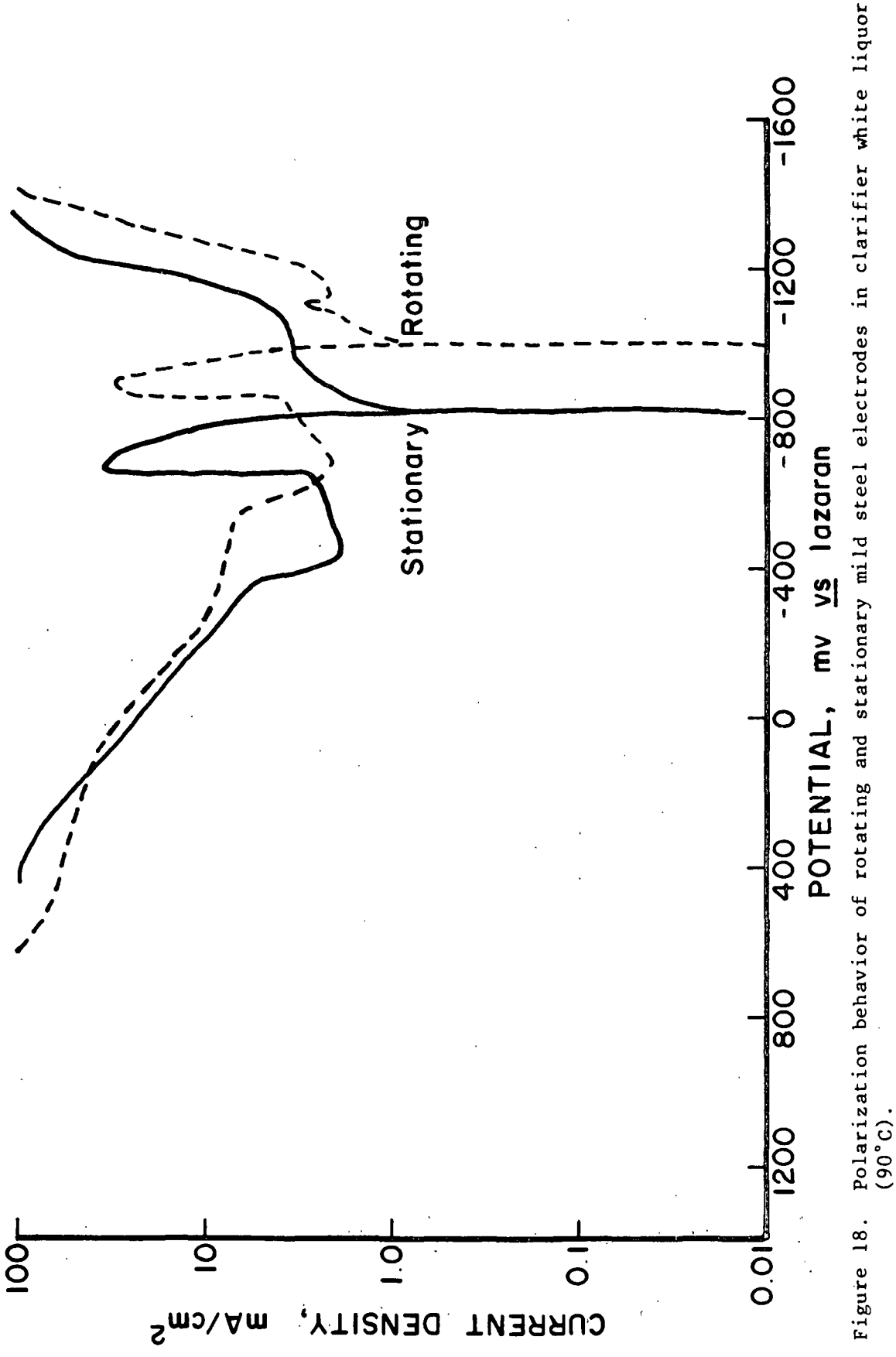

Figure 18. Polarization behavior of rotating and stationary mild steel electrodes in clarifier white liquor (90°C).

This preliminary test program was worthwhile, for it prepared us for the conditions and techniques required for future white liquor studies. However, it was not without problems. The major catastrophe was plugging of the plumbing and heater coil with suspended solids from the liquor. Since the presence of solids is necessary for erosion-corrosion measurements, a new simulator was constructed for continuous feed and discharge during testing. Another problem was reference electrode stability. The outer casing on these electrodes had deteriorated, allowing entry of liquor and poisoning of the cell. New casings are now in use which produce the required stability, and a new double junction-type of reference system is currently being evaluated. Rake construction and positioning had to be modified for proper contact in erosion and galvanic corrosion measurements. The new system to simulate white liquor clarification is shown in Fig. 19. Steel (55 gallon) drums with a alkyd/epoxy coating (Herosite) on internal surfaces were used to sample and transport the white liquor from four FKBG mills to IPC. These drums are Department of Transportation (DOT) approved for shipment of highly caustic liquids. The top of the drum contains ports to accommodate an agitator, barrel pump, inlet feed, and outlet plumbing (Fig. 19). The ports are designed for quick installation of pump/plumbing components to avoid liquor oxidation.

Figure 20 is a close-up view of the clarifier simulator. A timing system is connected to the inlet valve (lower left) and in conjunction with the outlet valve controls continuous circulation of the liquors. The pulley drive motor (upper left) is the prime mover for the rotation of the shaft and rake attachment (center, bottom) inside the insulated test cell (right center of photo). This system is all Teflon-Kynar construction.

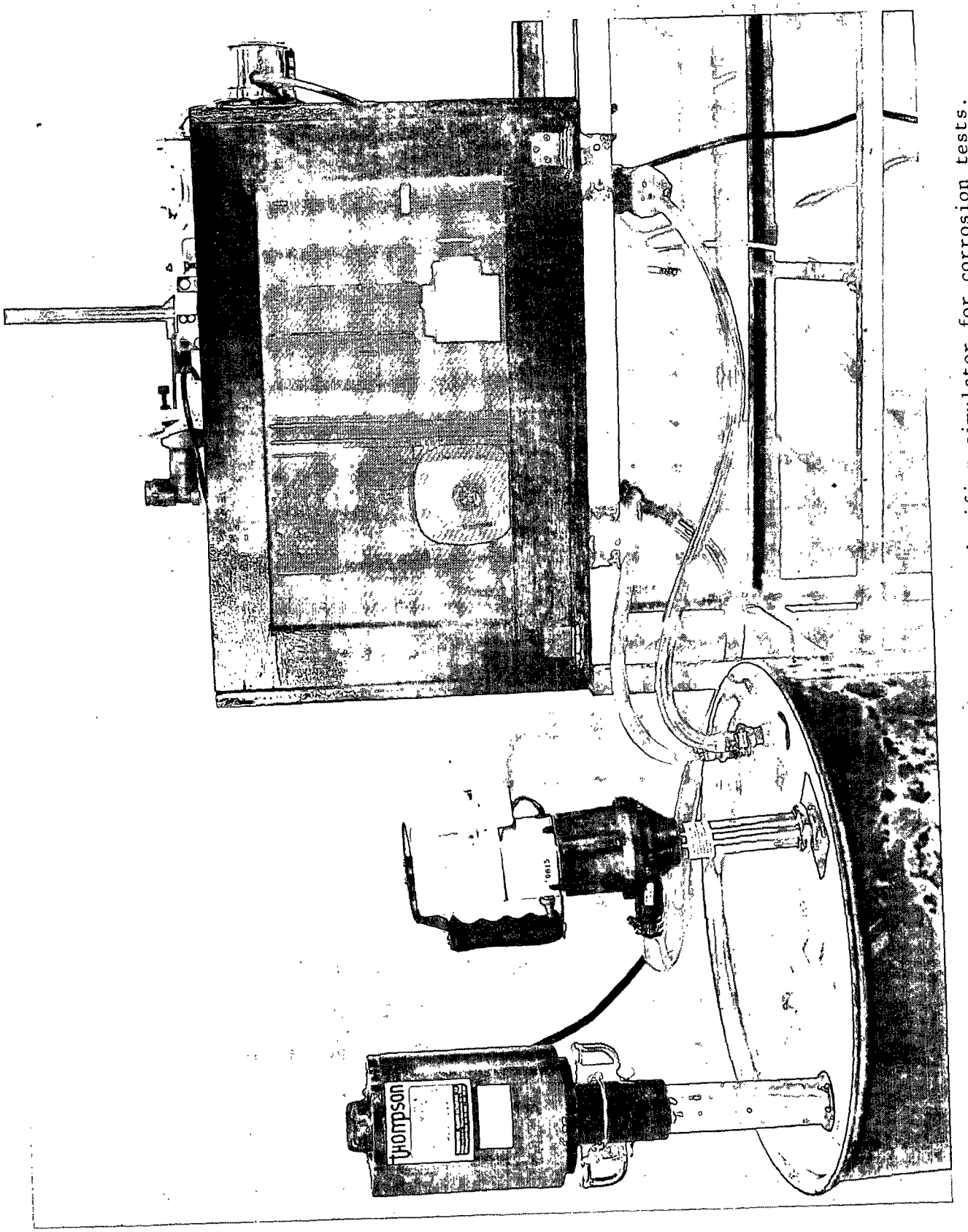

Figure 19. Photograph - overall view of white liquor clarifier simulator for corrosion tests.

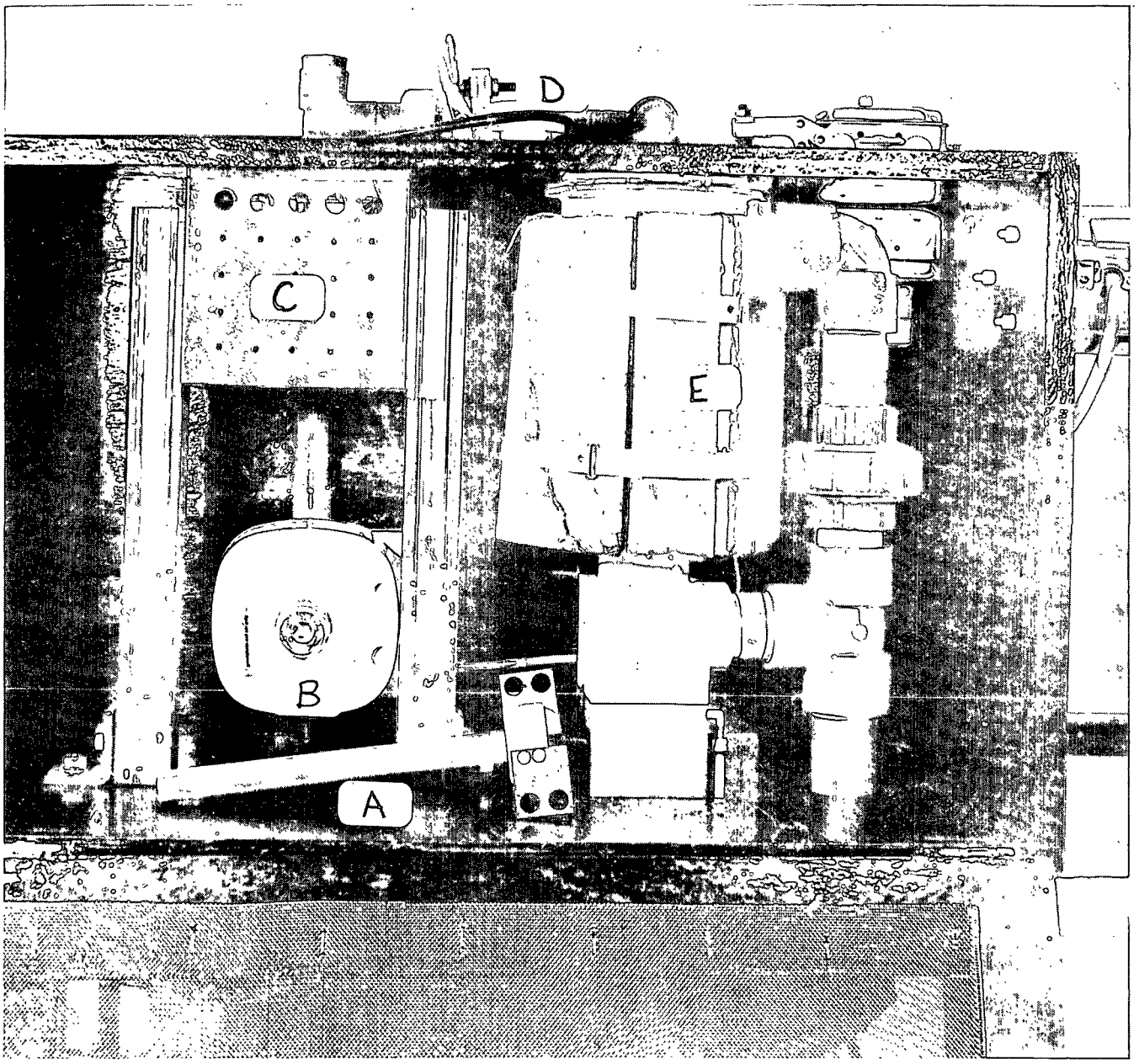

Figure 20. Close-up view of clarifier simulator.

A Shaft and rakes
B Time control valve - feed
C Drive motor for pulley D
D Pulley - sheave and belt
E Insulated Teflon corrosion cell

PHASE II - FKBG/IPC PROJECT 2926-6 (1980-1981)

White Liquor Corrosivity

Table III shows the analyses and corrosion test results for white (clarifier) liquors from four FKBG member company mills. Disregarding the polysulfide concentrations (analyses suspect due to analytical method), the highest corrosion rate (mill code No. 4) is, by comparison, associated with the highest thiosulfate and trace metal (Fe, Mn, Ni) concentrations and the lowest sodium sulfite concentration. Since that combination of analyses does not prevail for the other three liquors, which show both the same as well as much lower corrosion rates, this finding is significant and demands further verification in future studies. The liquor of highest chloride content is not associated with the highest corrosion rate. Furthermore, corrosion of mild steel weldments, i.e., welded rakes, was not enhanced compared with that of parent metal (mill code No. 14, Table III).

Polarization tests were conducted on mild steel in each liquor as received and pretreated (aerated, 15 minutes). Figure 21 shows the anodic polarization behavior of mild steel in all liquors as a banded curve and with labels A-B (passive region), C (primary passive potential and current), and D (corrosion potential). The dashed curve shows the typical behavior for aerated liquors (data shown from mill code No. 17). Table IV shows the magnitude of current and potential in each labeled region as well as a calculated corrosion rate based on the passive current density and a limiting current density from cathodic scans (not shown in Fig. 21). The latter data were to permit comparison of liquor corrosivity. Galvanic current measurements were also performed by coupling mild steel to Type 304 stainless steel in white liquor from mill No. 17. The tests were conducted at 90°C and with three different area ratios, mild steel to stainless. The results (bottom of Table IV) show a significant increase in galvanic action when the area ratio is 1:20.

TABLE III

CHEMICAL COMPOSITION[a] AND CORROSION RATE DATA FOR KRAFT WHITE LIQUOR

Item	Liquor, Mill Code Number 22	4	14	17
pH	12.8	13.0	13.0	13.1
Sulfide as Na_2S, gm/L	26.4	34.4	39.3	30.8
Sulfite as Na_2SO_3, gm/L	2.5	0.6	3.2	3.2
Thiosulfate as $Na_2S_2O_3$ gm/L	5.6	14.0	4.2	4.2
Polysulfide sulfur, gm/L	1.3	0.1	1.7	2.4
Iron, mg/L	2.9	10	1.2	0.8
Manganese, mg/L	3.3	4.8	0.6	3.2
Nickel, mg/L	0.8	0.7	0.7	2.4
Chloride, mg/L	2820	2620	3940	1500
Solids, %	19.0	22.7	27.1	20.5
Corrosion rate[b], mpy	2.5	51.2	13.9 (7, 4, weldments)	46.6

[a]Analyses performed by Badger Laboratories and Engineering.
[b]Corrosion rate (mpy - mils per year - 0.001 inch per year) was obtained by weight loss from duplicate tests on mild steel, rake-type coupons rotating (10 rpm) in white liquor for 200 hours.

In comparing the electrochemical and weight-loss corrosion data with the liquor analyses, there are several discrepancies. On a relative basis, electrochemical predictions of corrosivity are incompatible with weight-loss corrosion data (note last two data entries in Table IV). Regions A-B, C, and D change very little with significant changes in analyses. For example, the primary passive current (C value, Table IV) would be expected to increase substantially with higher thiosulfate, liquor No. 4 vs. other liquors, but this was not so. Also, the subtle changes in corrosion potential among various liquor compositions and with aeration were

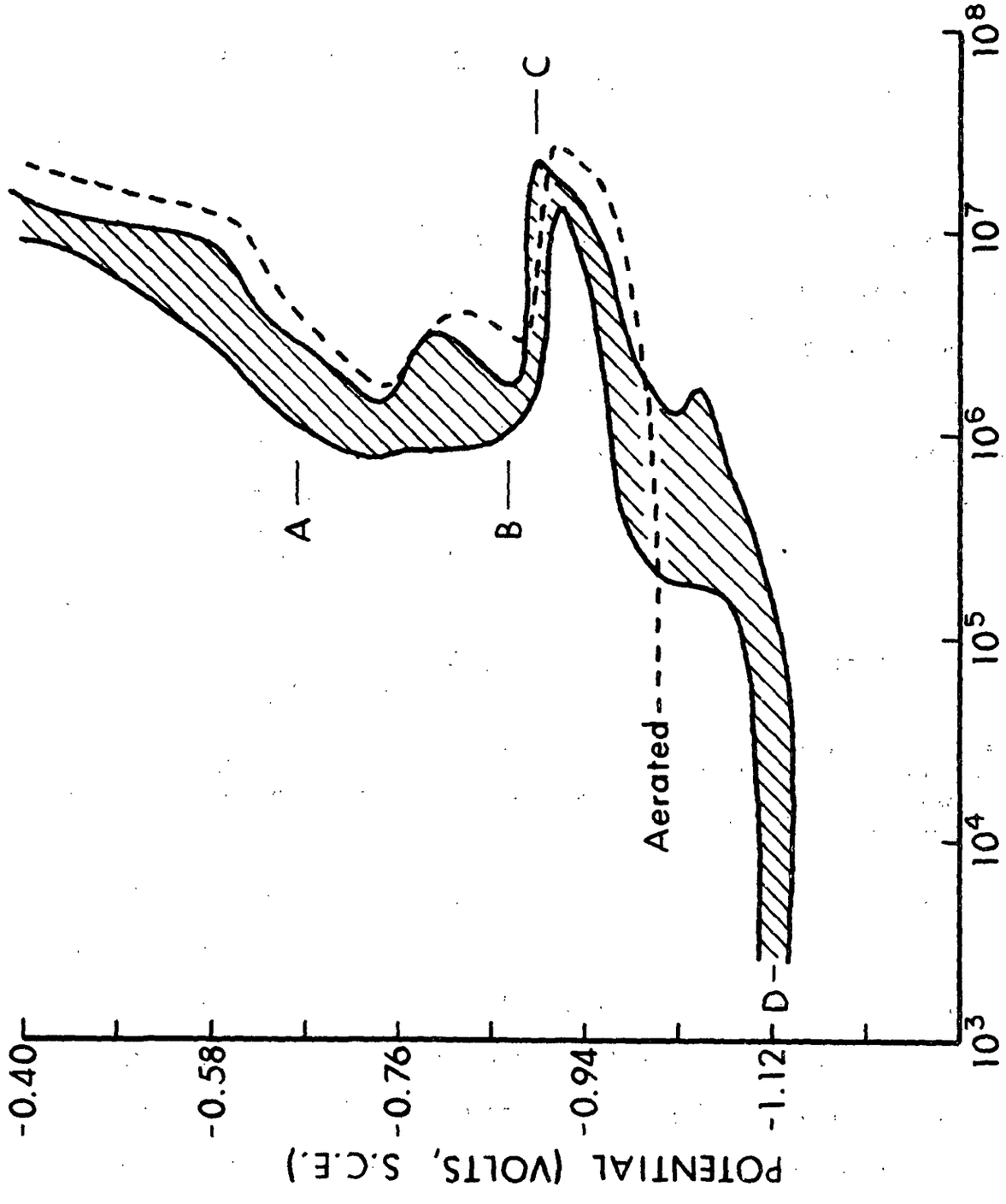

Figure 21. Polarization behavior of mild steel in white liquor - banded curve includes data from testing four liquors; dashed curve is typical for liquor pretreated by aeration.

unexpected. In view of these results and those by others, reported later in this paper, the future studies of white liquor corrosivity will primarily rely on weight-loss measurements.

TABLE IV

CORROSION DATA (POLARIZATION[a] AND WEIGHT LOSS)
FOR MILD STEEL IN KRAFT WHITE LIQUOR

Item	Liquor, Mill Code Number 22	4	14	17
Passive region, A-B, (mv, S.C.E.)	126	102	142	92
Primary passive current density, C, (μA)	16	19, (25, aerated)	17	23
Primary passive potential, C, (mv, S.C.E.)	-934	-926 (910, aerated)	-922	-905
Corrosion potential, D, (mv, S.C.E.)	-1140	-1048 (-1030, aerated)	-1028	-1056
Calculated corrosion rate, Region A-B, (mpy)	360	392	351	365
Calculated corrosion rate, cathodic, i_L, (mpy)	--	382	2260	152
Weight loss (from Table III, mpy)	2.5	51.2	13.9	46.6
Galvanic current density $\left(\frac{\mu A}{cm^2}, 90°C\right)$				
@ Area ratio - MS: 304 stainless: 1:1	--	--	--	250
1:10	--	--	--	280
1:20	--	--	--	500

[a]See Fig. 1 to identify points A, B, C, and D.

Weak Liquor Corrosion Tests

Initial tests were accomplished using weak black liquor obtained locally. To distinguish this liquor from that of FKBG mills in this report, this liquor is designated "E." Sampling location was the last stage or cleanest filtrate from

brown stock washing. The potential decay behavior (Fig. 22) indicates a stable, passive film buildup on both mild steel and Type 304 stainless steel. The mild steel surface was lightly encrusted with a corrosion product film which adhered in random locations upon washing after the test. The stainless steel surface was clean after exposure. The final steady-state potential after 60 hours of exposure (Fig. 22) indicates both metals are in the passive state as shown on the polarization diagrams obtained in subsequent tests (Fig. 23). Designated values of potential and current density, i.e., E_1, E_2--, I_1--, etc., shown in Fig. 23, as described for white liquor tests, were used to evaluate the effect of liquor age in testing. A summary of these values, typical for mild steel and Type 304, is shown in Table V. No significant difference was observed in behavior or appearance of these metals from the standpoint of the age of the liquor.

Upon completion of the above proof-tests, the evaluation of weak liquor supplied from FKBG member company mills was started. Mill (code) Number 22 sent liquors from filtrate tanks representative of initial and final brown stock washing. These liquor filtrates are designated as follows:

Liquor 22A - Approximately 5% solids weak liquor filtrate from initial washing of all softwood pulp

Liquor 22B - Approximately 5% solids weak liquor filtrate from initial wash of mixed hardwood-softwood pulp

Liquor 22C - Approximately 1% solids weak liquor filtrate from final wash of mixed hardwood-softwood pulp

Liquor 22D - Approximately 1% solids weak liquor filtrate from final wash of all softwood pulp

The analyses of these liquors, as well as liquors supplied by FKBG mill No. 15 and No. 21, are shown in Table VI. Total solids varied from 7 to 70 grams per liter depending on sample location as indicated.

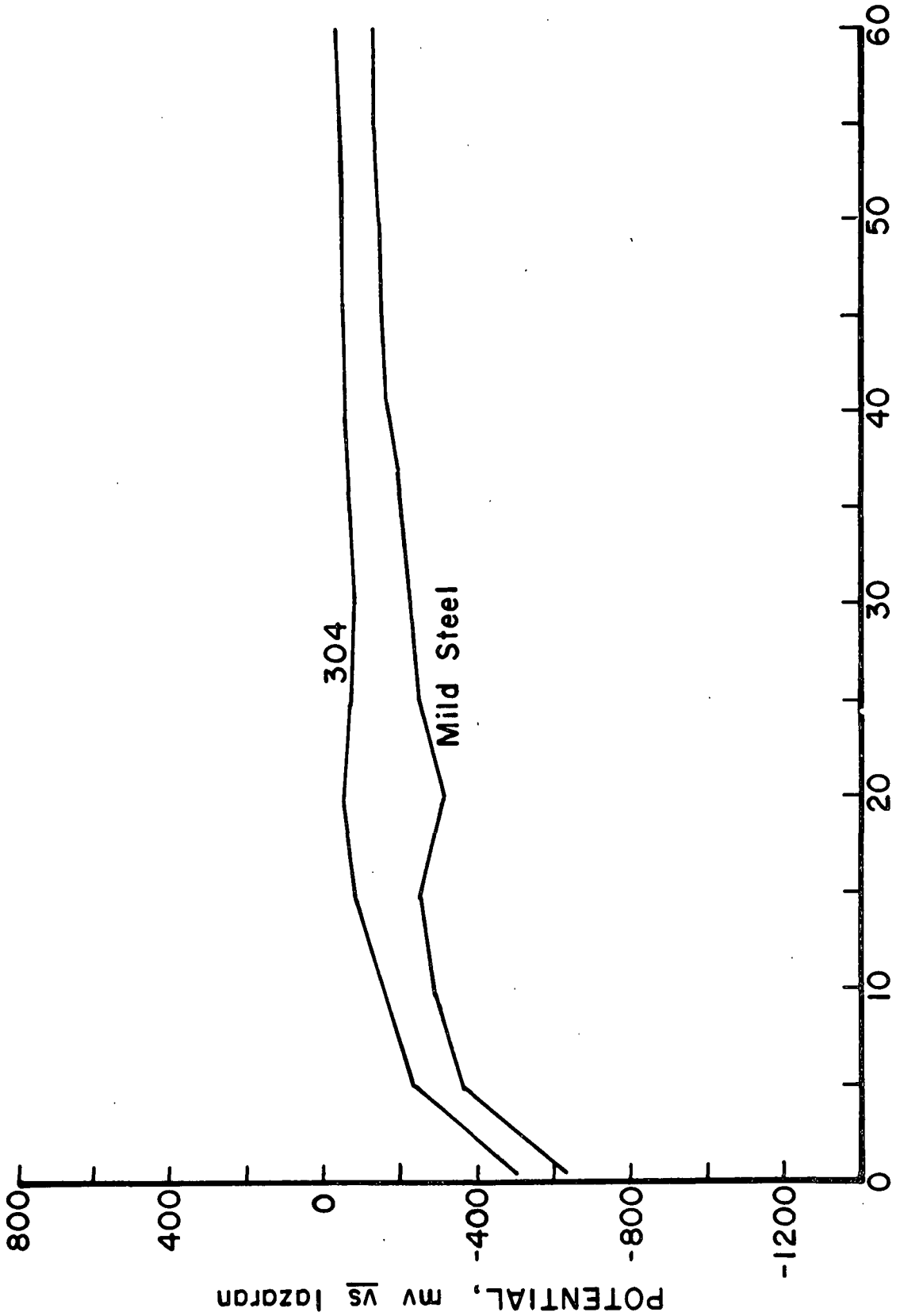

Figure 22. Potential decay of mild steel and 304 stainless steel in weak black liquor E.

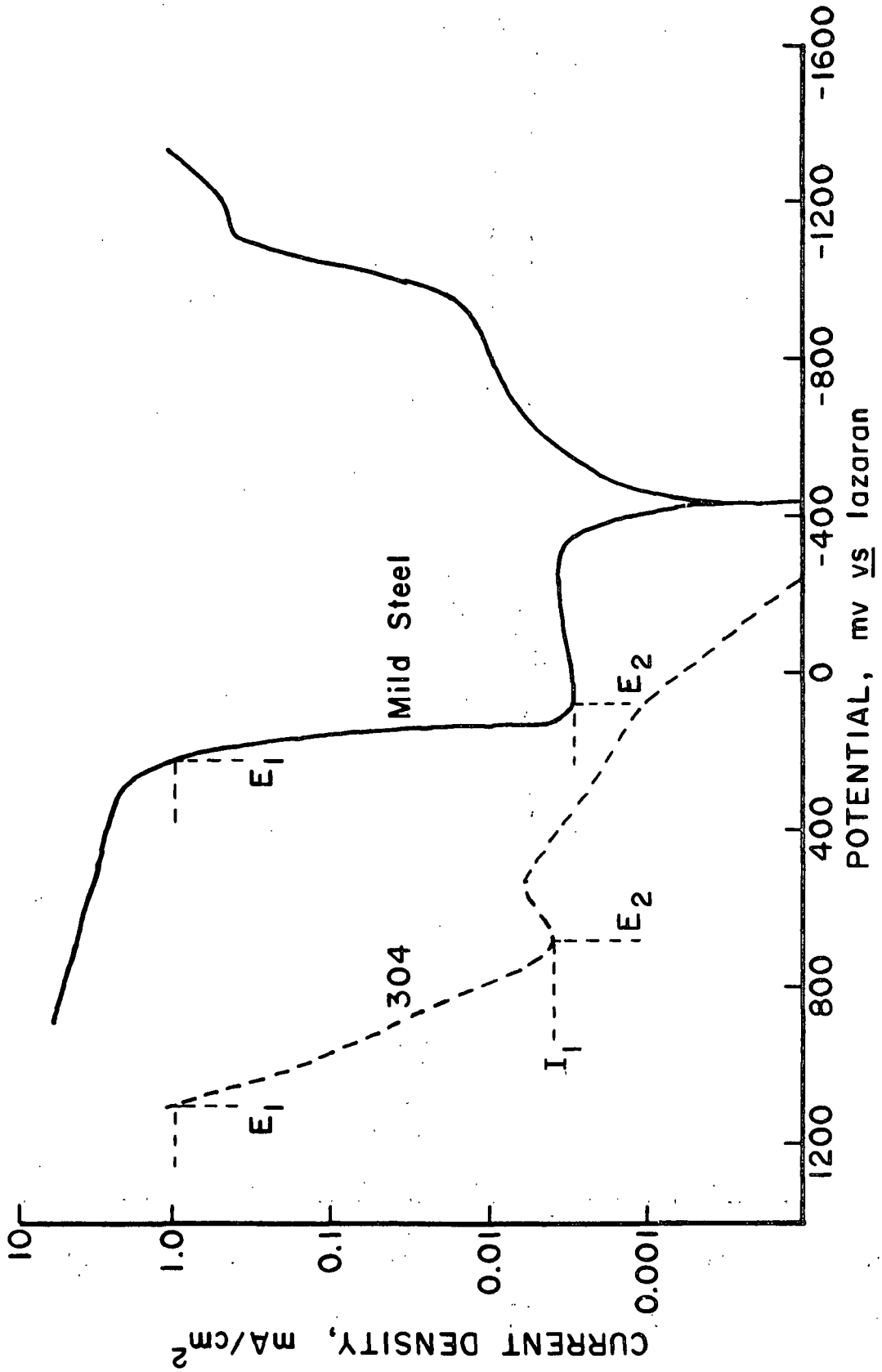

Figure 23. Polarization behavior of mild steel and 304 stainless steel in weak black liquor E (70°C).

TABLE V

ELECTROCHEMICAL POLARIZATION DATA FOR MILD STEEL AND TYPE 304 STAINLESS STEEL IN WEAK LIQUOR E

Run No.	Age (days)	Passive Range (mv., Laz.)	E_1 (mv., Laz.)	E_2 (mv., Laz.)	I_1 (mA/cm^2)
			Mild Steel		
1	2	644	+410	+160	0.027
2	9	1145	+1060	+680	0.014
3	11	975	+980	+560	0.012
4	41	910	+640	+430	0.009
			Type 304		
1	16	997	+1120	+640	0.006
2	16	948	+1140	+670	0.004
3	17	987	+1200	+660	0.010
4	40	1075	+1200	+700	0.005

Figure 24 shows the potential decay behavior for mild steel in first-stage brown stock washer filtrate (≈ 45 g/L solids). These results indicate stable corrosion product buildup regardless of liquor composition. The brown to black surface appearance after 60-hour exposure was removed on cleaning except at random locations. Surface attack at the latter locations was insignificant. Kraft liquor 22A and B results are compared with 21D; the results for 21D are for a mixed kraft semichemical liquor, yet there is no difference in behavior. The interpretation of results for mild steel weldment potential decay in these liquors, shown in Fig. 25, is the same as just described. In fact, the behavior for different liquors is almost identical.

TABLE VI

WEAK LIQUOR PROPERTIES

Mill Liquor Code Number	Sample Location (BSW)[a]	pH	Conductivity	Density, g/cm^3	Na_2S, mg/L	Total Solids, g/L	Na_2SO_3, mg/L	$Na_2S_2O_3$, mg/L
15A	3rd Stage	11.21	12,860	1.008	<1	16.1	30	330
21B	1st Stage (semi-chemical)	7.56	39,400	1.030	55	70.1	None detected	394
21C	1st Stage (kraft)	11.04	26,000	1.018	28	45.6	71	897
21D	Mix (9:1) (21C:21B)	10.65	29,000	1.018	28	47.8	Not analyzed No sample provided	
22A	1st Stage (base)	12.18	23,400	1.018	<6	47.1	25	533
22B	1st Stage (liner)	12.02	19,020	1.017	<6	41.8	None detected	431
22C	2nd Stage (base)	11.89	8,410	1.003	7	10.6	4	75
22D	2nd Stage (liner)	11.71	6,080	1.000	<6	7.84	--	49
E	2nd Stage	--	--	--	--	8.38	17	168

[a]BSW - Brown Stock Washer.

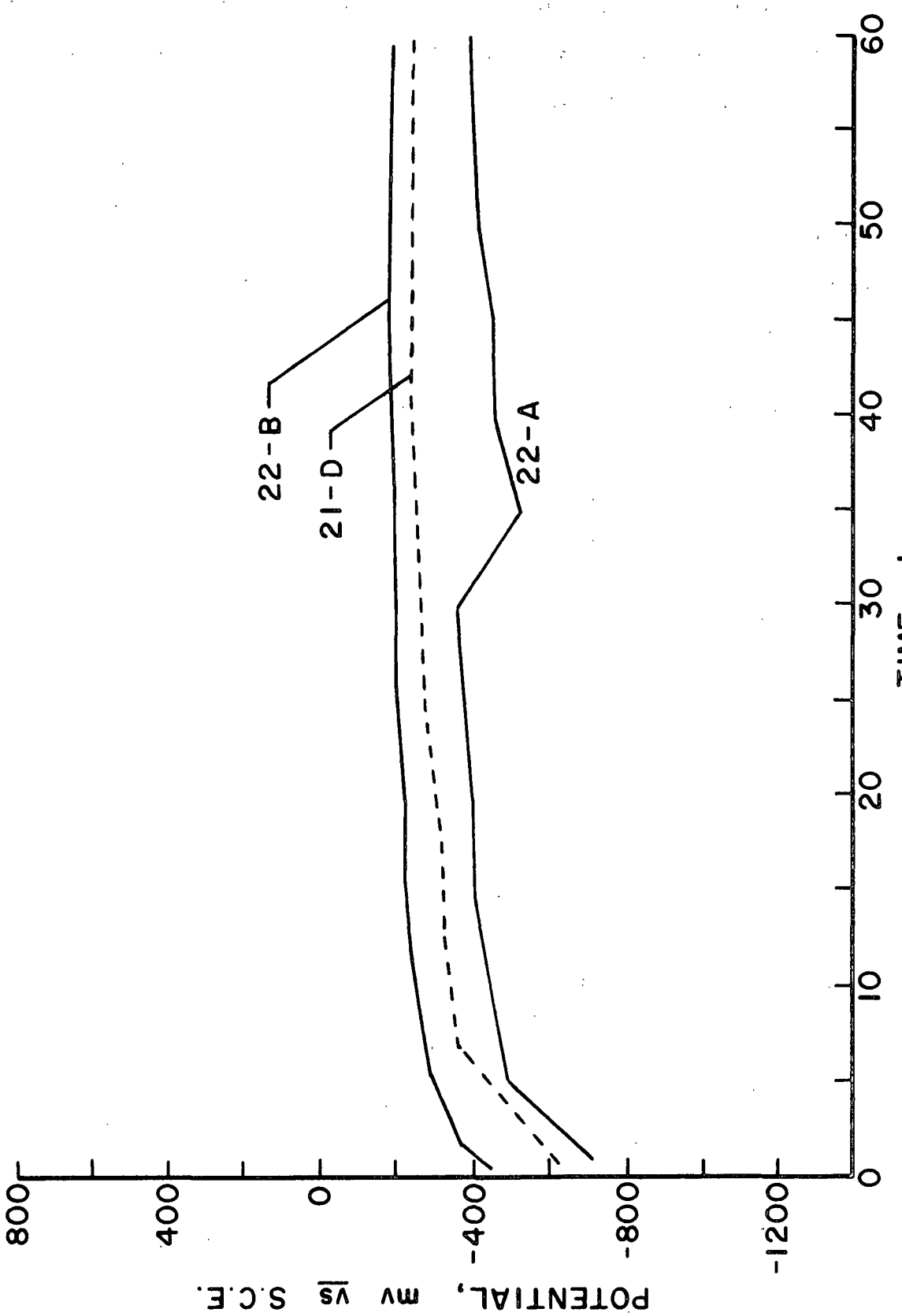

Figure 24. Potential decay of mild steel in weak black liquor at 45 g/L TS and 60°C.

Potential decay results for Type 304 stainless steel and its weldments for the 45 g/L solids liquor are shown in Fig. 26 and 27. These metals remained clean and passive throughout the exposure period as indicated by the potential measurements.

The potential decay data for all liquors on each metal were replotted to identify trends in this behavior as a function of solids content. No consistent relationships were determined, so these data are omitted.

The polarization behavior of mild steel and its weldment in the 45 g/L solids black liquors is shown in Fig. 28 and 29, respectively. In all liquors, these metals show a delayed buildup of (passive) corrosion product film as the applied anodic potential is increased. This is indicated by the "humps" in the curves over a range of -400 to +400 mv, S.C.E. Film growth is apparently inhibited with applied potential by heavier solids liquor. However, the corrosion rate achieved after development of a stable film is similar for all liquors.

The corrosion associated with final film breakdown at the completion of the test is restricted to local sites of attack at small deposit/film buildups. These buildups are observed on the mild steel surfaces in decay (exposure, unpolarized) tests, but these are observed to be more highly concentrated in applied potential tests. The buildup accumulations are occasionally more extensive in coverage over the test specimen surfaces exposed to polarization tests, and these have also been observed on the bottom of the corrosion test cell. These accumulations are believed to be the same as those reported by the mills as deposits in filtrate tanks.

The anodic polarization behavior of Type 304 stainless steel and weldment in the 45 g/L solids liquors is shown in Fig. 30 and 31, respectively. These curves indicate slight changes in passive film composition by the breaks in the curves at

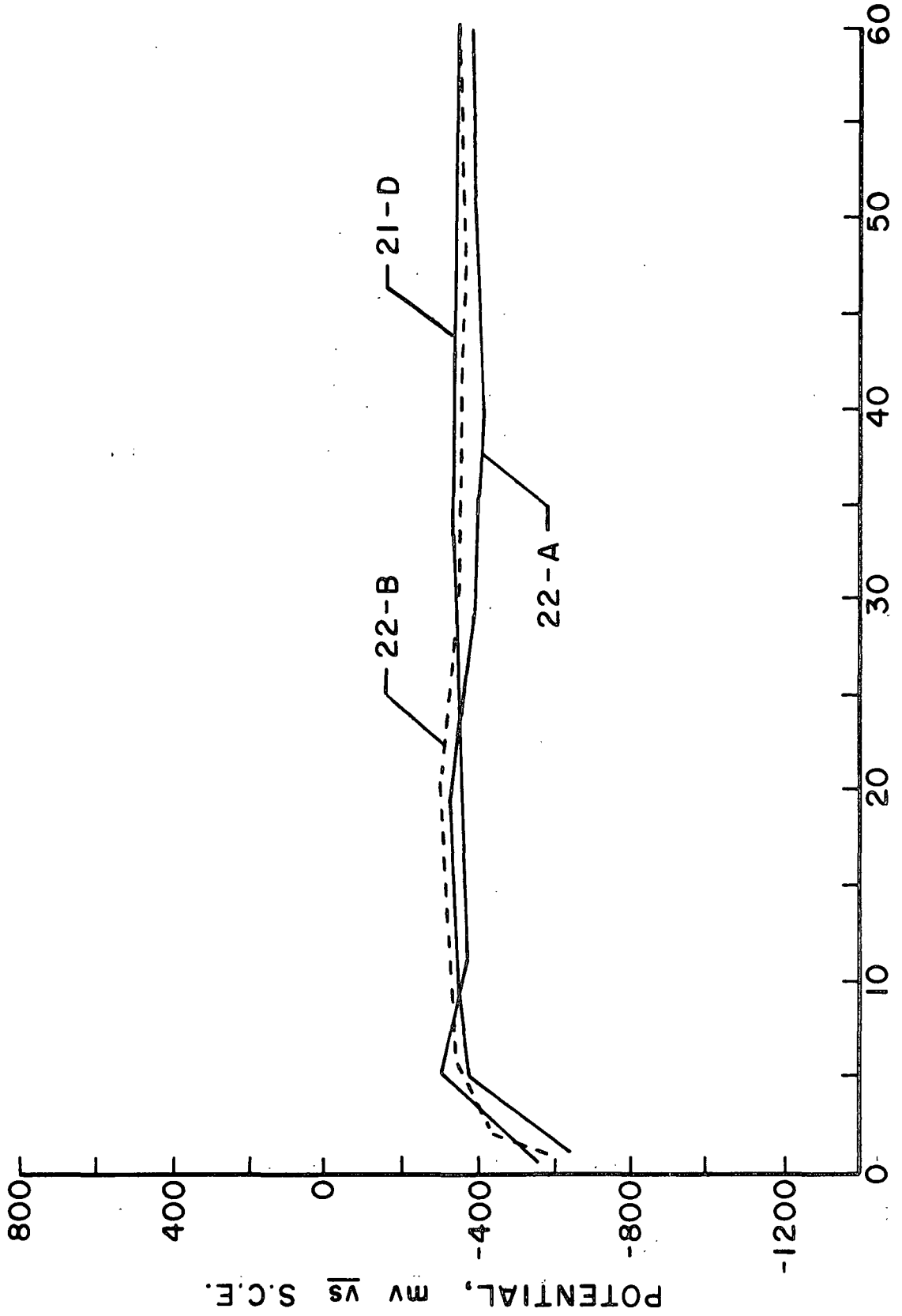

Figure 25. Potential decay of MS weldments in weak black liquor at 45 g/L TS and 60°C.

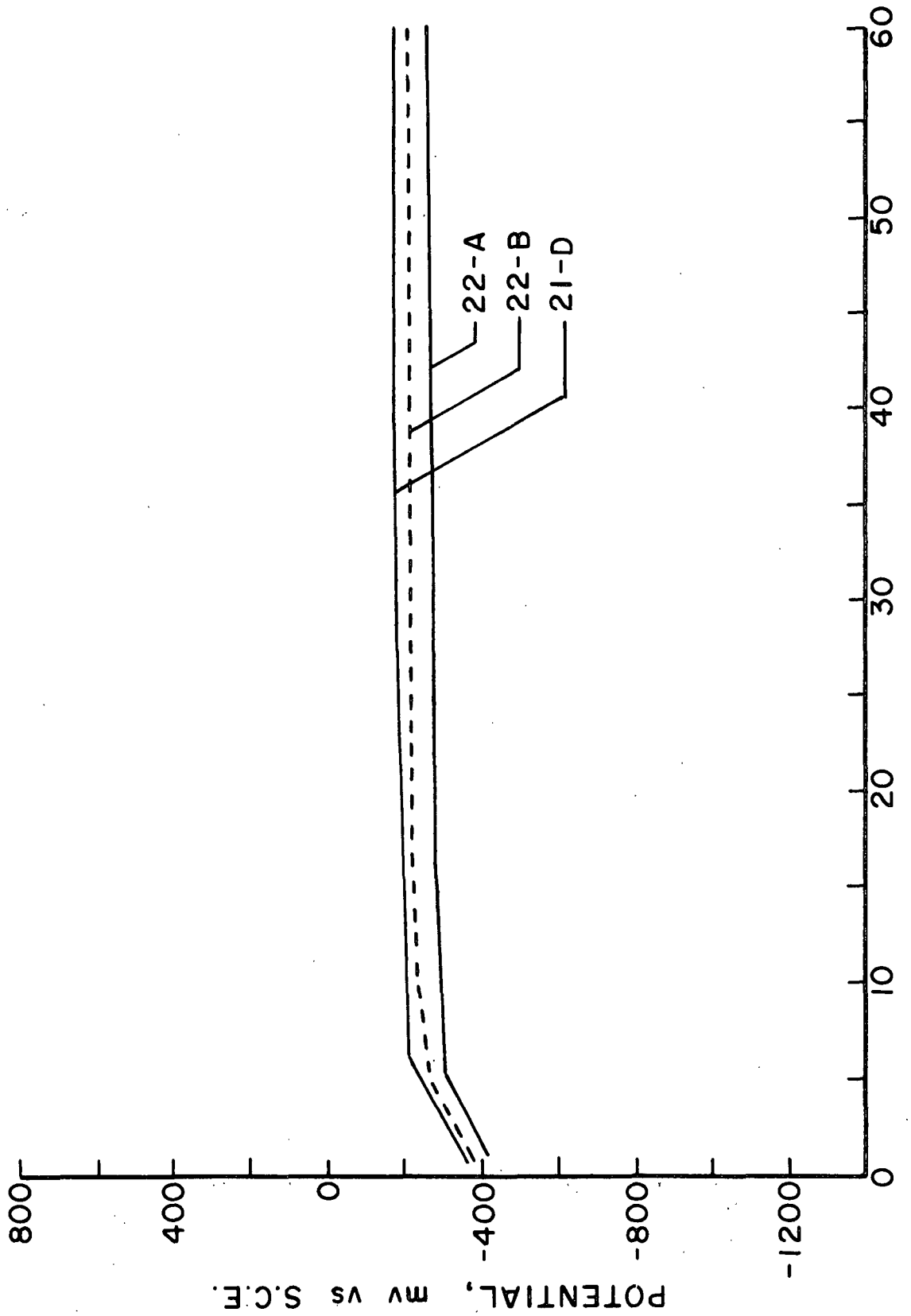

Figure 26. Potential decay of 304 SS in weak black liquors at 45 g/L TS and 60°C.

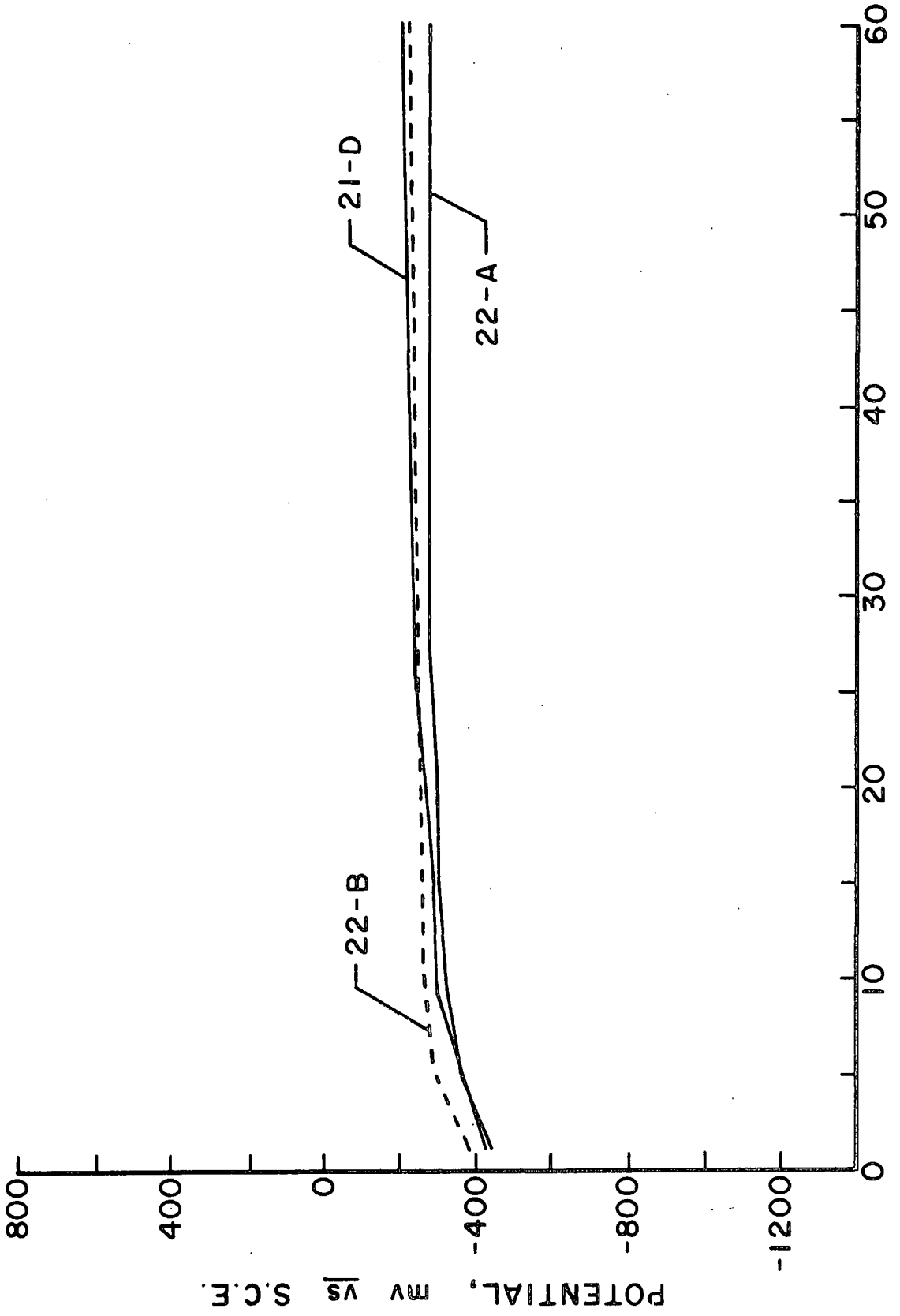

Figure 27. Potential decay of 304 SS weldment in weak black liquors at 45 g/L TS and 60°C.

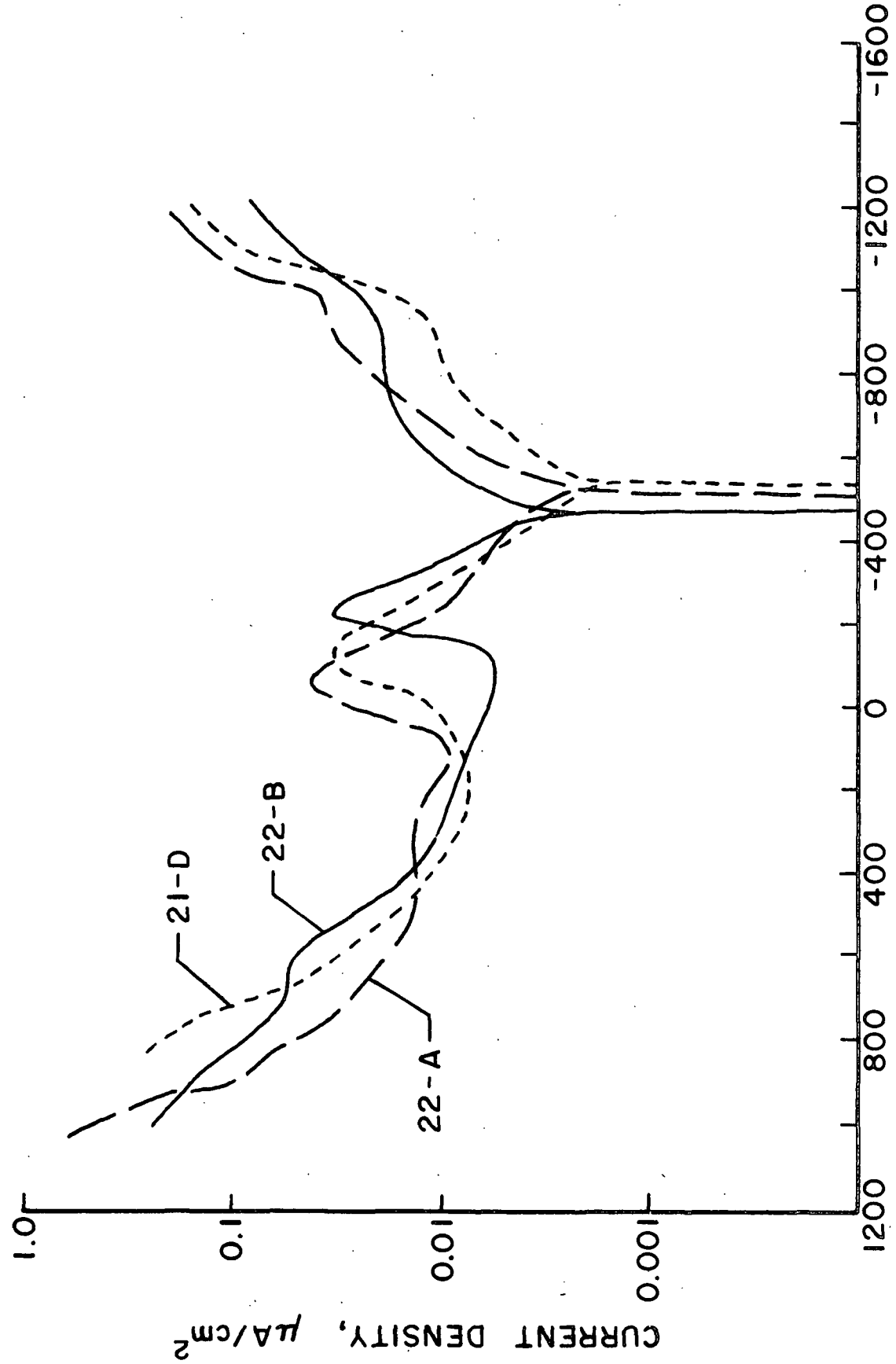

Figure 28. Polarization behavior of mild steel in weak black liquors at 45 g/L TS and 60°C.

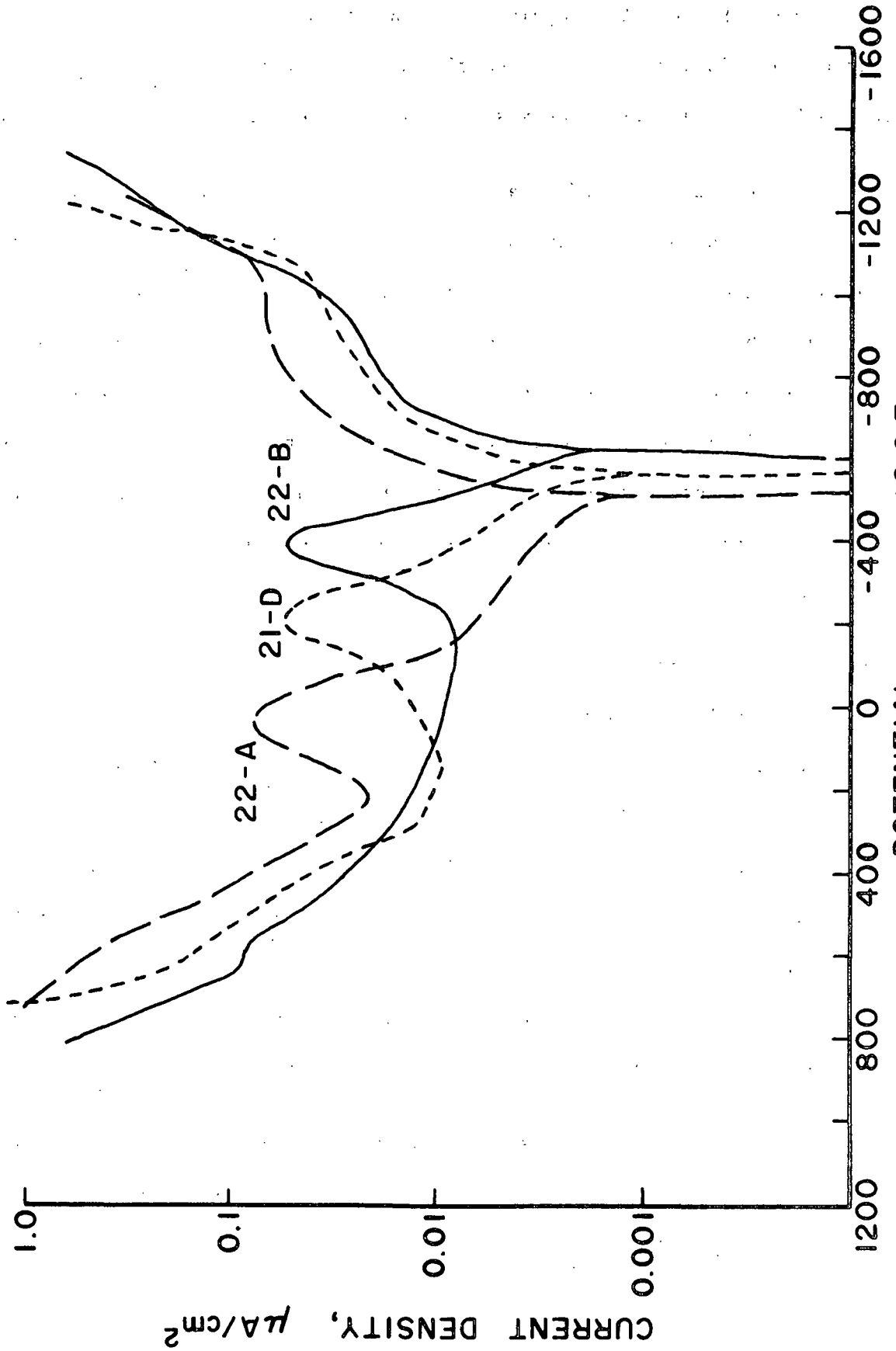

Figure 29. Polarization behavior of mild steel weldments in weak black liquors at 45 g/L TS and 60°C.

≈ -200 and +500 mv, S.C.E., but consistently low corrosion rate of the metal. The coupon surface also is indicative of the film change by slight discoloration. No significant difference in corrosion was observed between liquors on these metals.

Comparisons were made of polarization test results for each metal as a function of solids content. In contrast to comparisons of potential decay results, these data show higher current density levels (more corrosion) and less stable passivity with higher solids liquor, i.e., first-stage brown stock washer filtrate more corrosive than second or third stage. In the case of mild steel and weldment, Fig. 32 and 33, this is considered to be the result of buildups, mentioned above, which are more predominant in the heavier filtrate. This effect is also apparent in the comparison of polarization curves for stainless steel and weldment, Fig. 34 and 35, though less pronounced.

Polarization tests were conducted with mild steel in representative weak liquors from three mills to evaluate the effect of increased temperature (+20°C) and aeration (5 minutes with oxygen just prior to testing). Figures 36 and 37 show the results for weak liquors of lowest solids content. Aerated liquors shifted the corrosion potentials of mild steel toward more noble (more positive) potentials and lowered the oxidation kinetics of metal/liquor systems with applied anodic potentials. The latter was especially true for the liquor containing sodium sulfide (Fig. 37). Higher temperature liquors favored more active rest potentials for mild steel and lower oxidation kinetics with applied anodic potentials.

The same temperature effects are indicated for higher solids (heavier BSW filtrates) liquors (Fig. 38-40); however, aeration had mixed effects. For the aerated kraft liquors (Fig. 38-39), the shift in corrosion potential was toward the active direction, and the oxidation kinetics (current rise as a function of applied

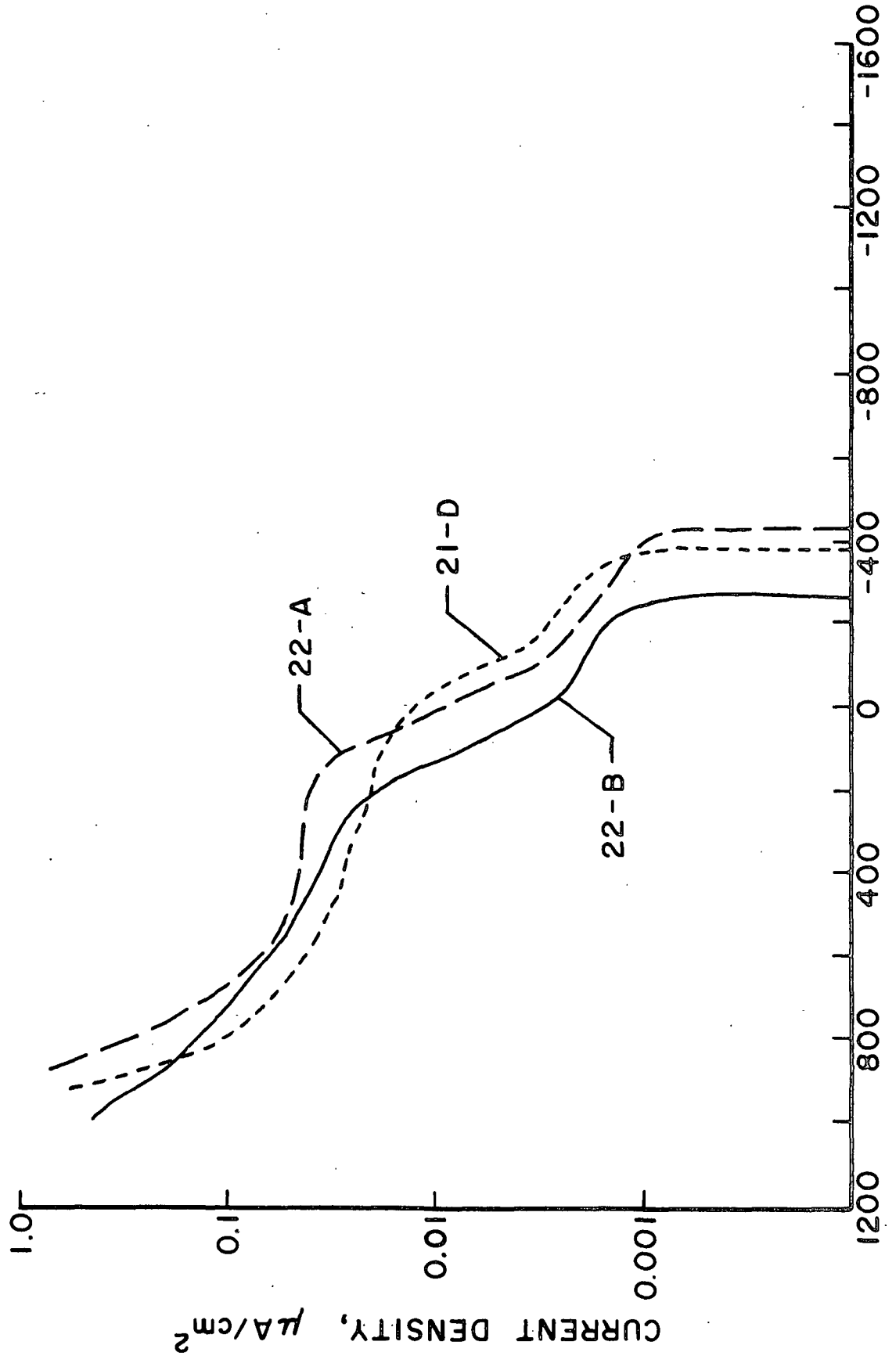

Figure 30. Anodic polarization behavior of 304 SS in weak black liquors at 45 g/L TS and 60°C.

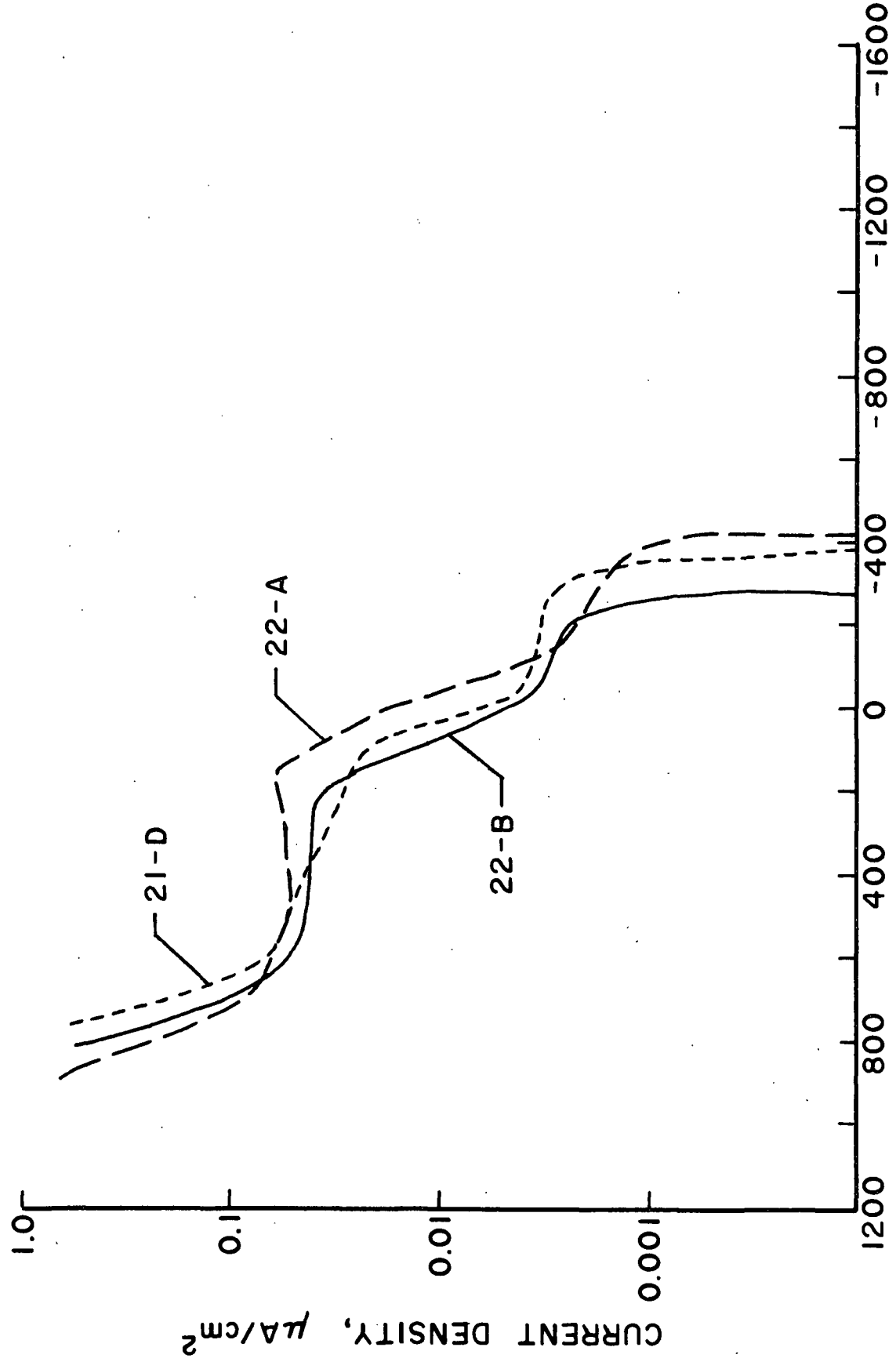

Figure 31. Anodic polarization behavior of 304 SS weldments in weak black liquors at 45 g/L TS and 60°C.

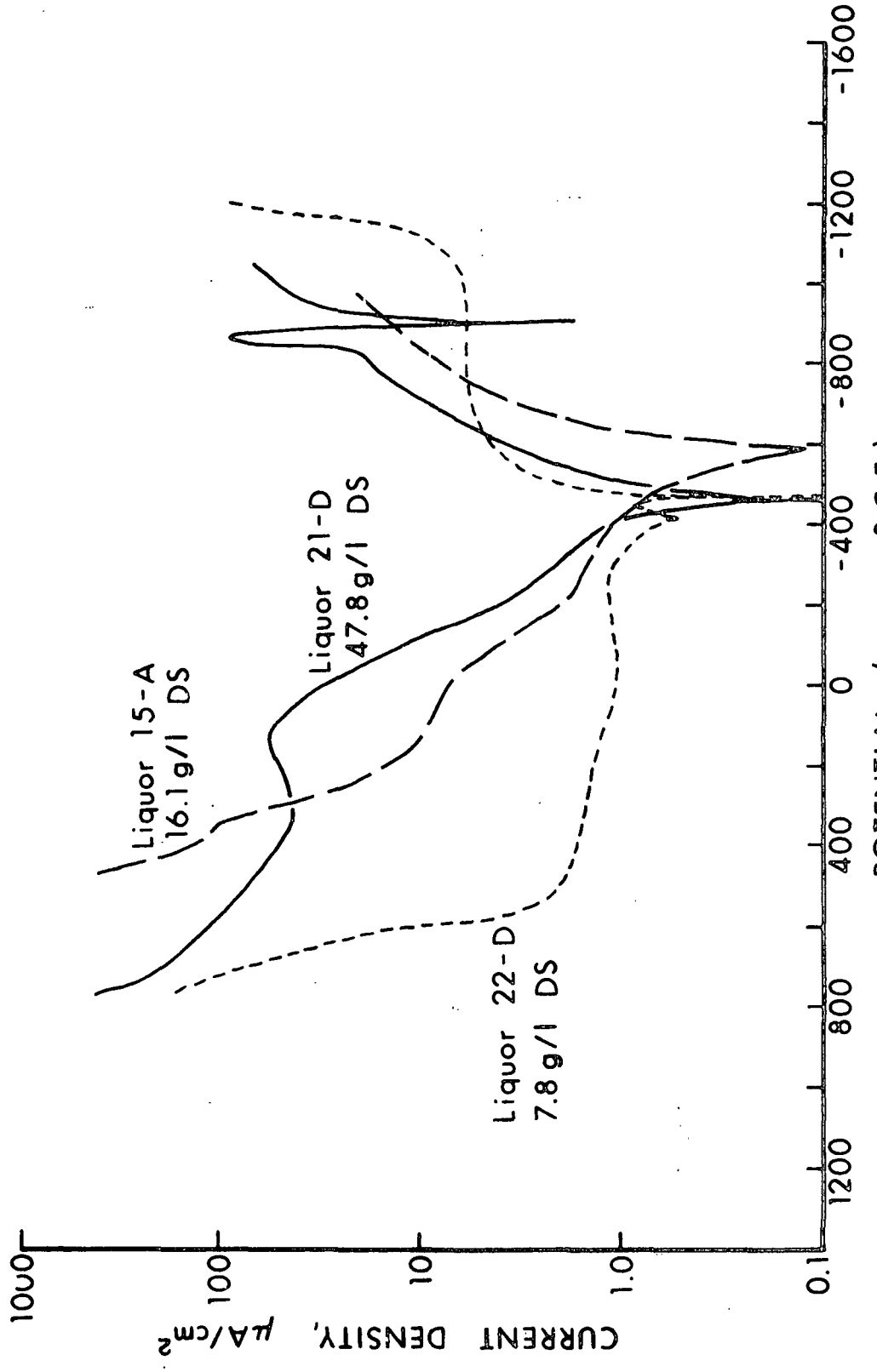

Figure 32. Polarization behavior of mild steel in weak black liquor - 60°C.

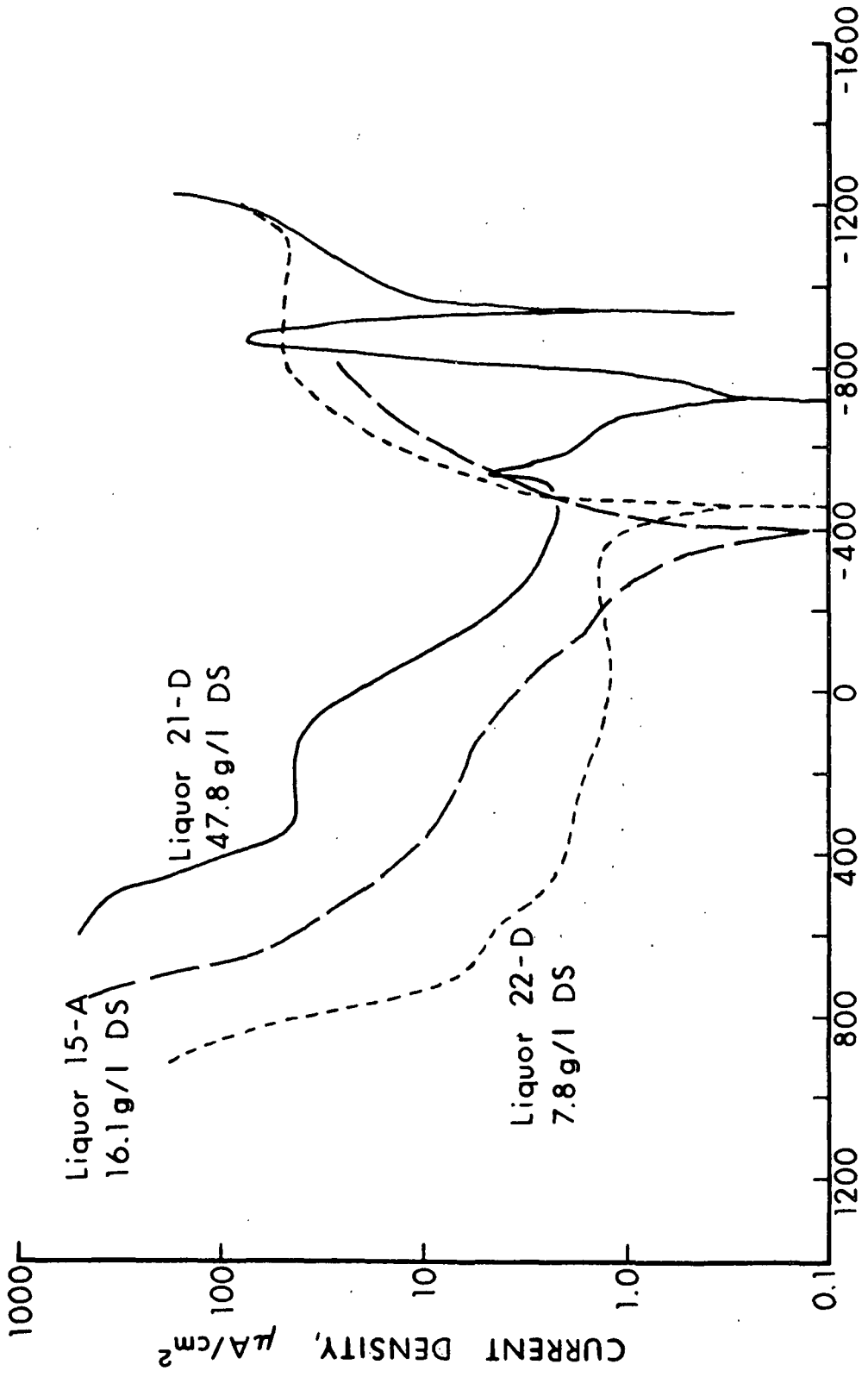

Figure 33. Polarization behavior of mild steel weldments in weak black liquor - 60°C.

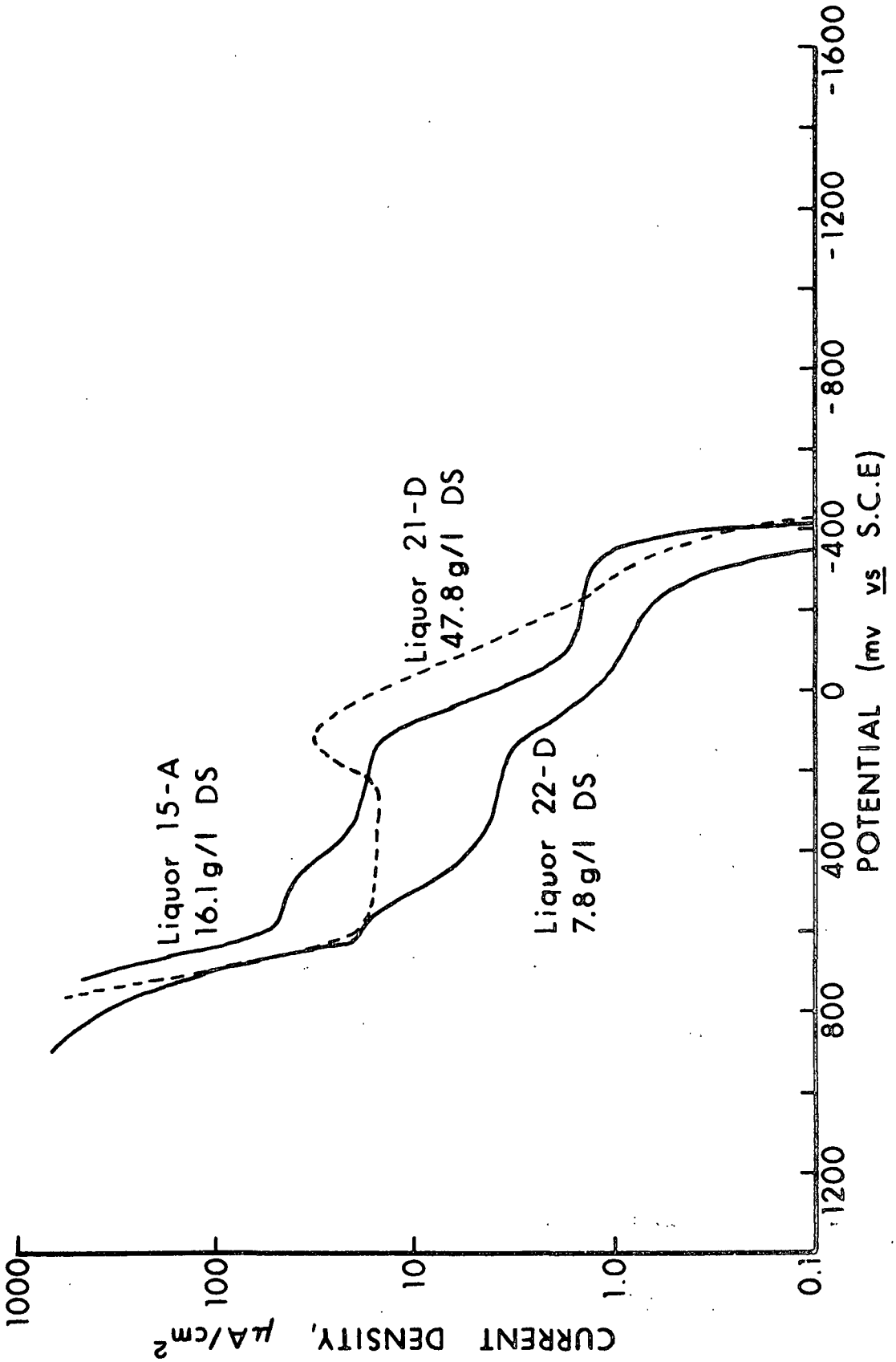

Figure 34. Polarization behavior of 304 stainless steel in weak black liquor - 60°C.

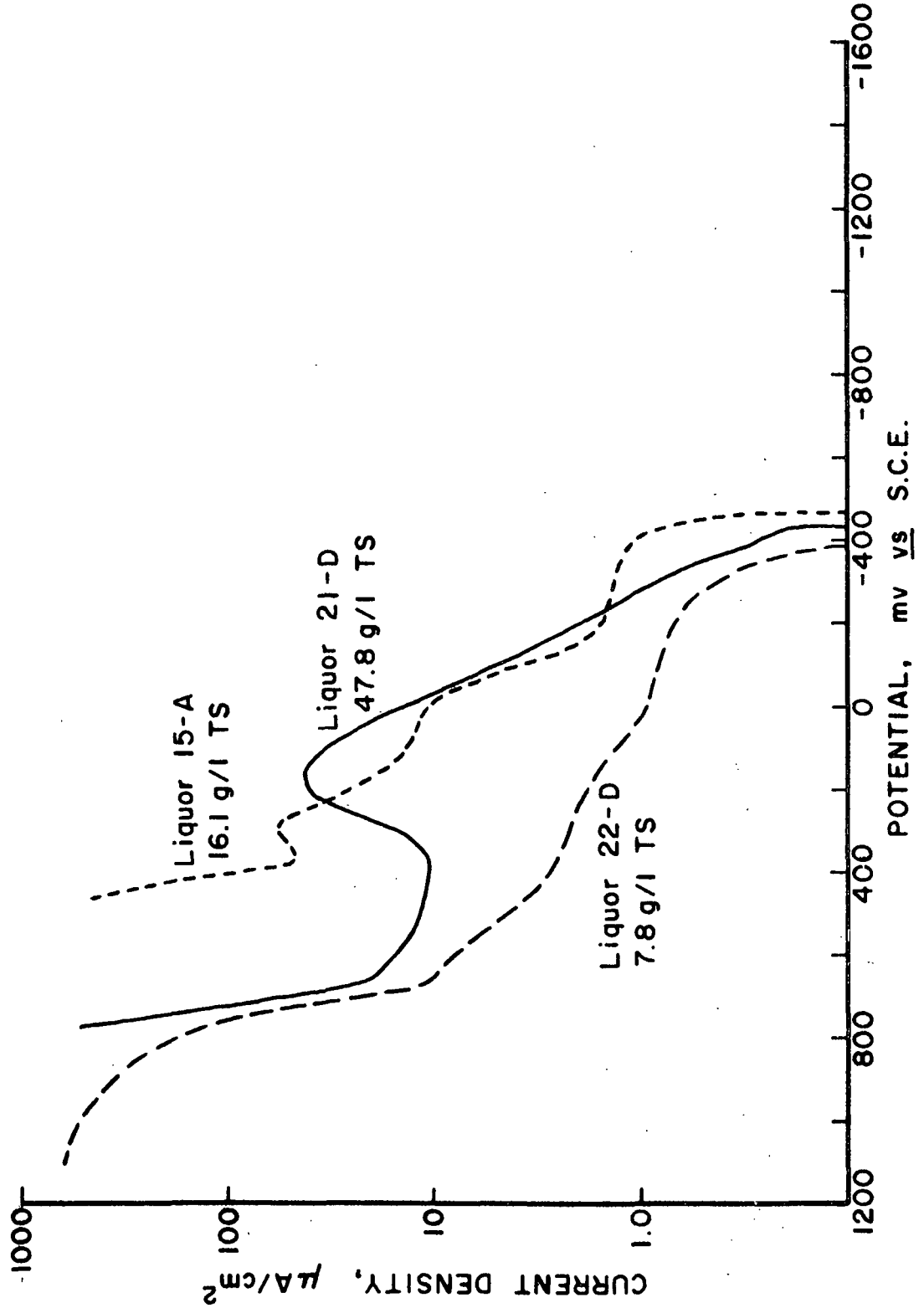

Figure 35. Polarization behavior of 304 weldments in weak black liquor at 60°C.

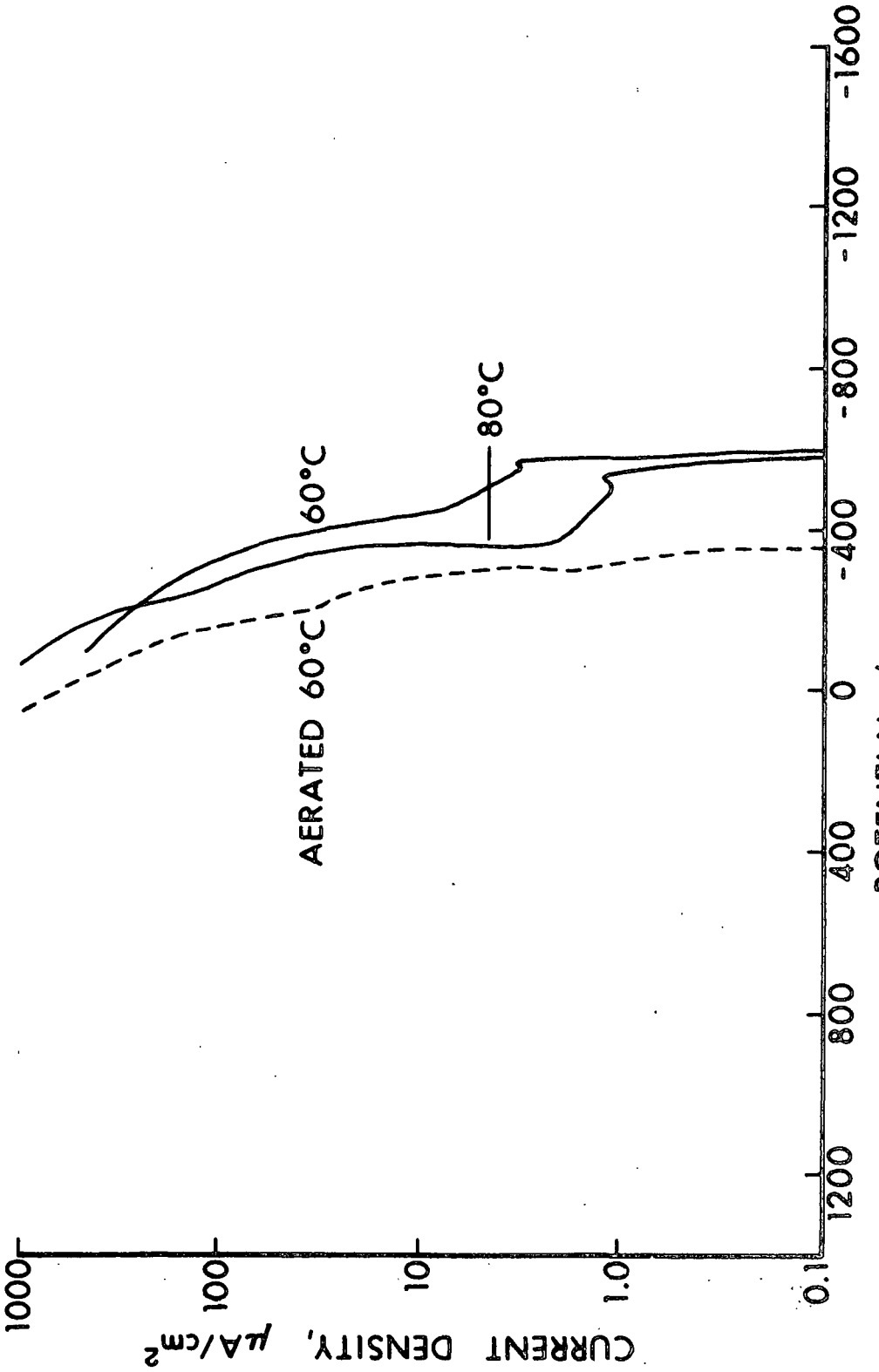

Figure 36. Anodic polarization behavior of mild steel in weak liquor 15-A (16.1 g/L solids, <1 g/L Na_2S, third stage BSW).

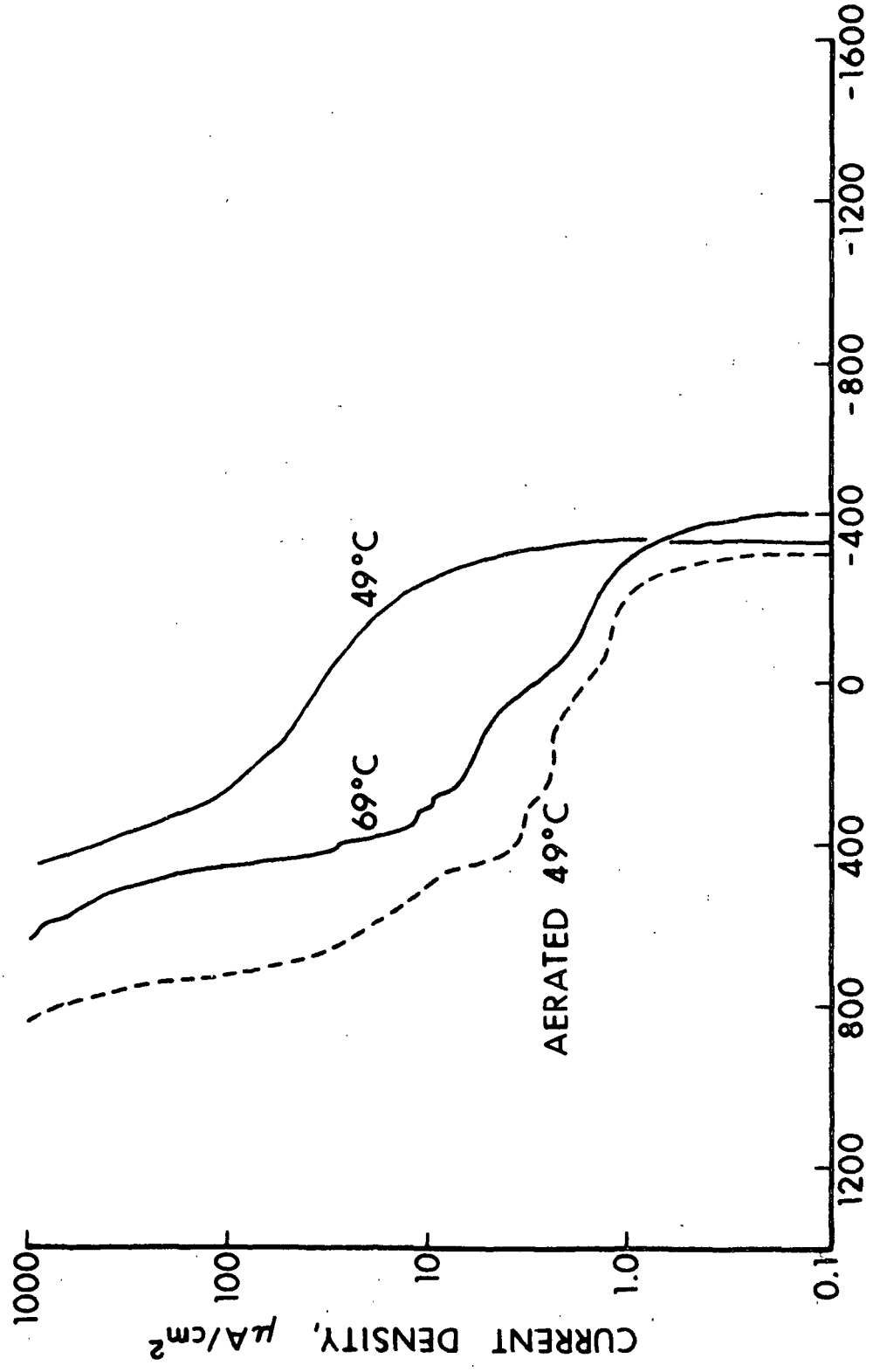

Figure 37. Anodic polarization behavior of mild steel in weak liquor 22-C (10.6 g/L solids, 7 g/L Na_2S, second stage BSW).

potential) were higher in one case (Fig. 38) and lower in the other (Fig. 39). This could be related to liquor composition or test conditions. Aeration effects in the kraft-semichemical liquor (Fig. 40) were similar to those reported for the lower solids liquor (Fig. 36-37).

In general, stainless steel specimens were free of attack by weak liquor, and the corrosion rate of mild steel was very low. The attack which occurred on mild steel was associated with deposits. Several attempts were made to "capture" these deposits for chemical analyses. A small amount was obtained from both the mild steel specimen surface and the corrosion test cell in testing liquor 21C. The analyses are shown in Table VII. The corrosion products are mainly composed of unidentifiable iron sulfur compounds, whereas the deposit in the bottom of the test cell is chiefly calcium carbonate.

Heavy Black Liquor Corrosion Tests

Two mills (Code No. 18 and 21) supplied heavy (55% solids), unoxidized black liquor for analyses and corrosion testing. The test materials were exposure (weight loss) tested in the liquid, vapor, and alternate liquid-vapor liquor environments simultaneously by a specimen holder containing nine specimens. We call the holder a "Christmas-tree" rack (see Fig. 41). Three specimens - parent metal, good, and bad weldments - were exposed at the three locations in each liquor.

Alternate liquor/vapor exposure tests were conducted on mild steel and weldments in two heavy black liquors. Specimens were exposed in the vapor and liquor as well as 50 alternate exposures to vapor/liquor during 288 hours of exposure. The corrosion rate results (Table VIII) show liquor 21 is more corrosive than liquor 18, but all weight-loss measurements were extremely low. The consistent result of higher vapor phase corrosion is considered to be caused by the difference in exposure of a

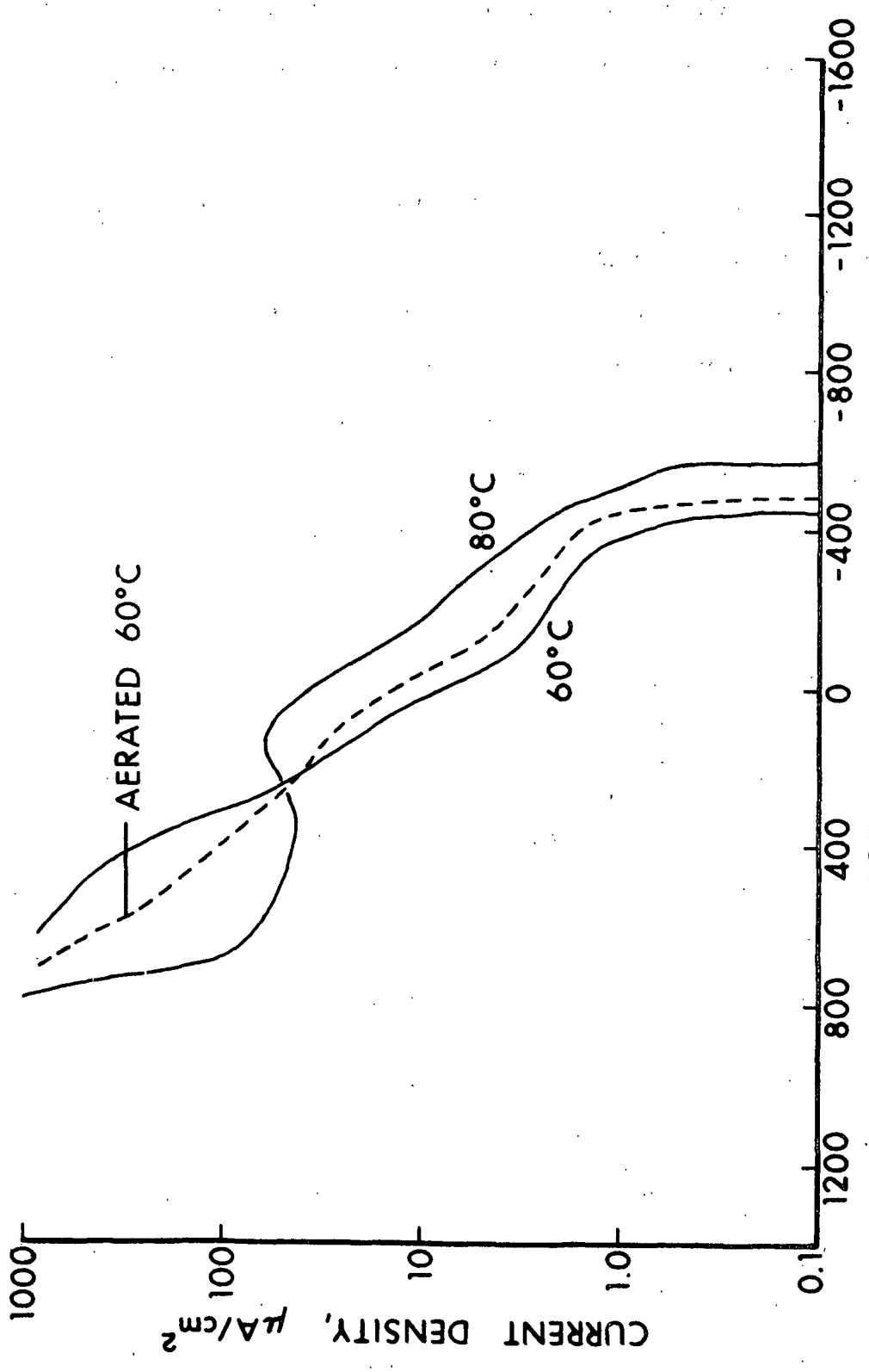

Figure 38. Anodic polarization behavior of mild steel in weak liquor 21-C (45.6 g/L solids, 28 g/L Na_2S, first stage BSW).

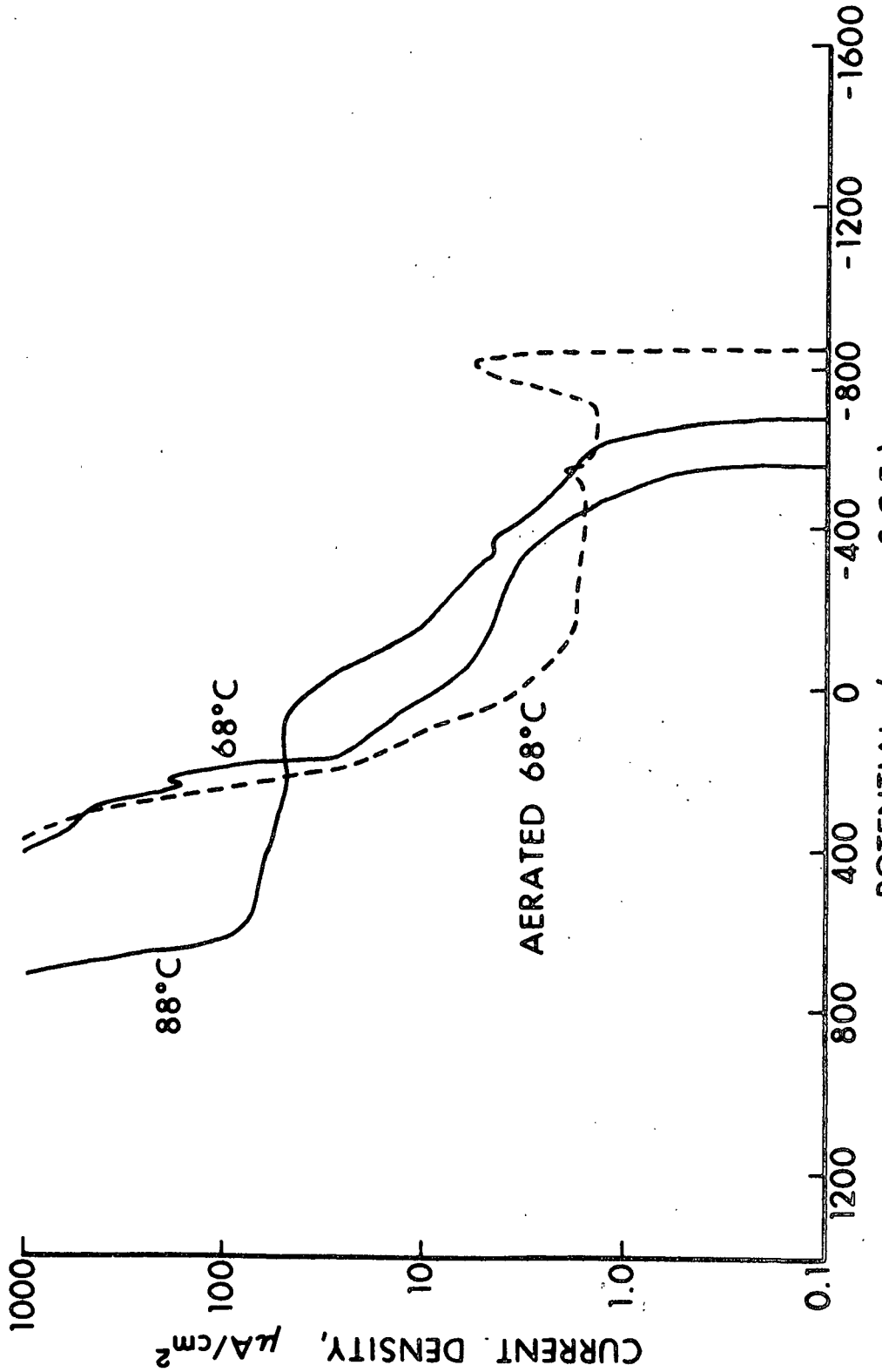

Figure 39. Anodic polarization behavior of mild steel in weak liquor 22-A (47.1 g/L solids, 28 g/L Na_2S, first stage BSW).

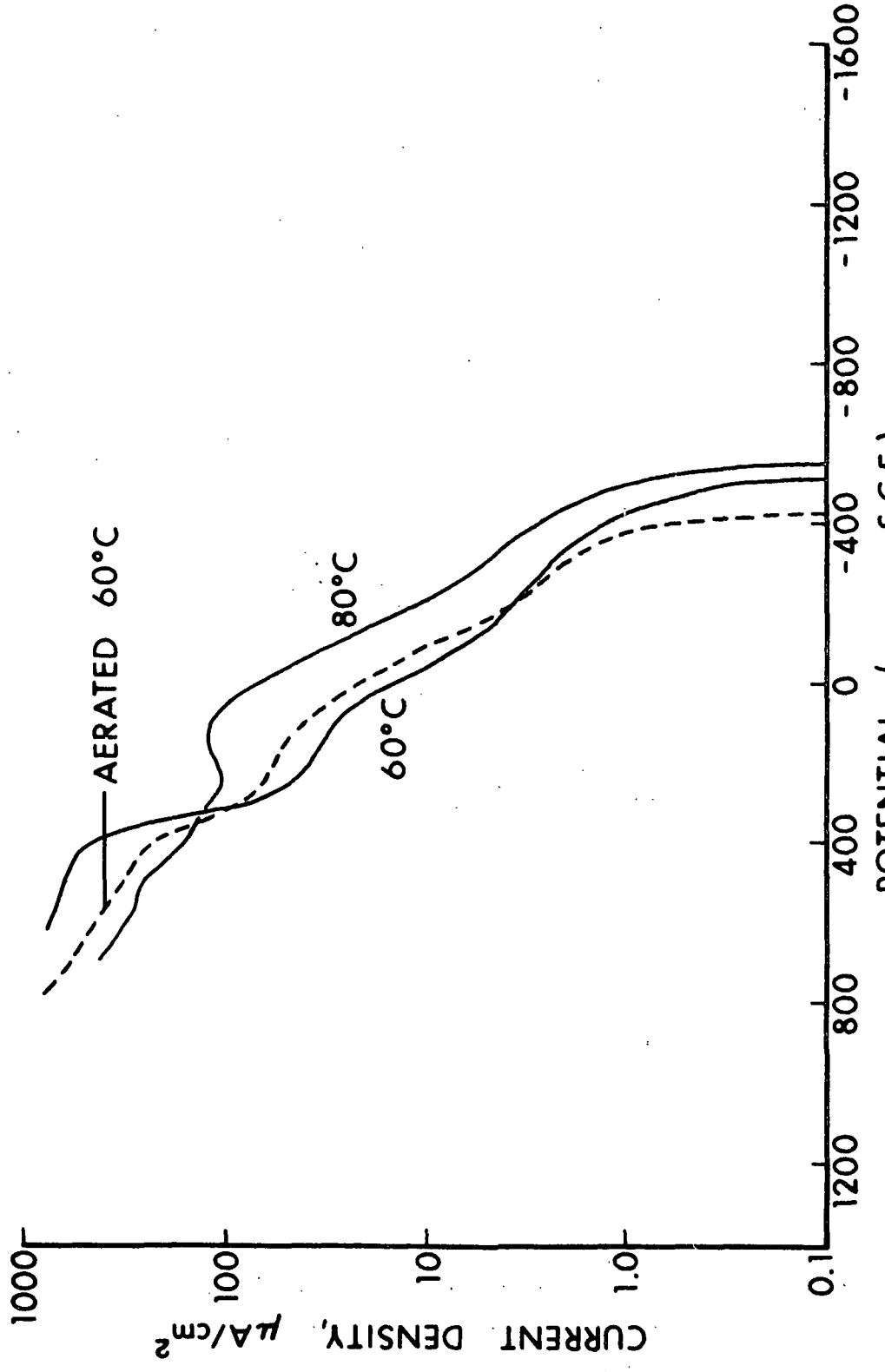

Figure 40. Anodic polarization behavior of mild steel in weak liquor 21-D (47.8 g/L solids, 28 g/L Na_2S, first stage BSW kraft:semichemical mix-9:1).

bare metal to the condensate as opposed to one completely coated with hot, thick black liquor, i.e., alternate exposure coupon.

TABLE VII

ANALYTICAL INVESTIGATION OF WEAK LIQUOR DEPOSITS AND MILD STEEL CORROSION PRODUCTS[a]

Kraft Liquor Filtrate 21C, First Stage BSW

Sample Type	Analytical Method	Major Constituents Determined
Deposit in bottom of corrosion cell	X-ray diffraction	Amorphous, calcium and carbon-major components, iron, silicon, sodium aluminum- small amounts
	Infrared spectrum	Calcium carbonate-major constituent
Corrosion products	X-ray diffraction	Iron and sulfur-major component, noncrystalline material
	Electron microprobe	Iron and sulfur are major constituents with small amount of carbon
	Infrared spectrum	Material largely inorganic, but did not match iron-sulfite, sulfate, oxide, or sulfide spectra

[a]Analyses performed by Walter C. McCrove Associates, Inc., Chicago, Illinois.

Subsequently, corrosion tests were performed on mild steel in condensate collected by vacuum-evaporation of liquor No. 21. Tests were also conducted in the same condensate mixed with 10% solids (taken from solids remaining after evaporation). Table IX shows the properties of condensate and mix as well as the corrosion rates. The corrosion rates are substantially higher than the 1 to 2 mils per year, reported previously for mild steel in this liquor, i.e., liquor/vapor tests. The solids impart a higher corrosivity to the condensate despite the pH increase. Since these electrochemical measurements are calculated corrosion rates at or near the corrosion potential, further verification is required by weight loss - exposure tests.

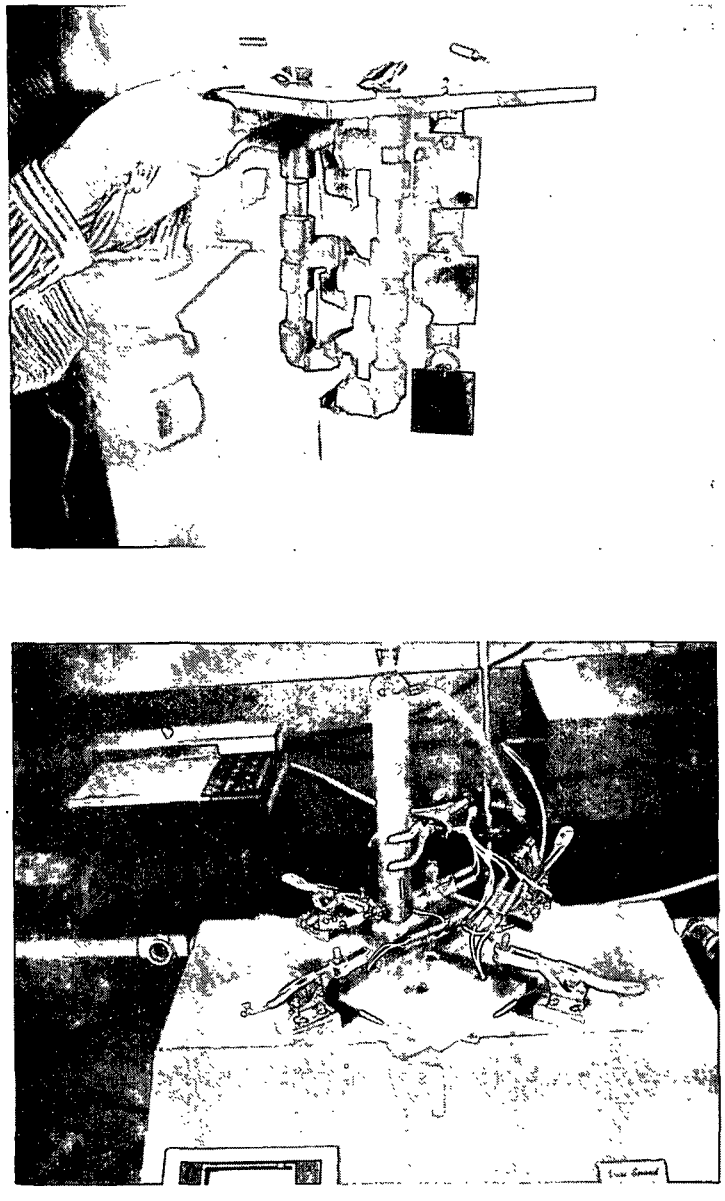

Figure 41. Photographs of "Christmas-tree" specimen holder for parent and weld metal coupons spaced to allow immersion for liquid, vapor, and alternate liquid/vapor exposure. Top photo - rack assembly; bottom photo - rack in place in autoclave.

PHASE III - FKBG/IPC PROJECT 2926-6 (1981)

The Phase II corrosion test program was completed in 1981. Several conclusions regarding this kraft liquor testing program became apparent. The use of

mill-supplied liquors restricted assessments of chemistry effects on corrosivity. In fact, the determination of liquor chemistry was questionable, and it became a separate coproject. The low corrosion rate results in weak and heavy black liquor, supplied by mills having corrosion problems in these systems, also indicated that other process variables, not included in this study, were important. The need for a better test technique became apparent. The evaluation of white liquor corrosivity also indicated the need for more accurate liquor analyses; this segment of the study was also limited to corrosion of rotating specimens. In view of these and other factors, a Phase III program was initiated to pursue better definition of the effects of chemistry and process conditions on corrosion. The detailed plans for this program are described in the final section of this report. Two aspects of this plan were developed by the end of 1981, and these are reported below.

TABLE VIII

CORROSION RATES (MPY) OF MILD STEEL AND MILD STEEL WELDMENTS IN KRAFT HEAVY BLACK LIQUOR AT 90°C[a]

Mill Code No.	Liquor Exposure			Alternate Liquor/Vapor			Vapor Exposure		
	Parent Metal	Good Weld	Bad Weld	Parent Metal	Good Weld	Bad Weld	Parent Metal	Good Weld	Bad Weld
18	0	0	0	0	0	0	0.43	0.43	0.16
21	2.45	2.37	2.16	0.56	0.07	0.26	1.74	0.95	1.05

[a]Corrosion rates in mils per year were measured by weight loss after 288 hours exposure; alternate liquor/vapor 5 times per 24 hours.

Stress-Related Corrosion Effects

Among the causative factors for enhanced corrosion, the effect of stress was considered important. Six pulley-weight systems were used to apply constant load(s) to mild steel rods immersed in weak, black liquor. Table X shows that very little corrosion is imparted to mild steel by applied stress levels up to 3000 psi

in as-received liquor. Table XI shows more significant corrosion rates of mild steel under 2000 psi stress in weak liquor containing high chloride. The data in Table XI reflect the need for better reproducibility, since some differences in rates are apparent. Figure 42 shows the corroded appearance of the rod specimens used in these tests. Figure 43 shows rod(s) appearance after removal of corrosion products (Cl tests, Table XI). The arrows in these photographs indicate the location of the cell fittings to the rod specimen. Crevice corrosion is apparent in these areas, and work is under way to either control this attack or make it consistent from test to test.

TABLE IX

HEAVY BLACK LIQUOR[a] AND CONDENSATE DATA

Item	Liquor	Condensate	Condensate + Mix
Total sulfur, %	3.99	--	--
Total solids, %	50.8	--	10
pH	--	8.5	12.2
Corrosion rate (mpy)	2.4	4.0	13.0

[a]Mill Code No. 21.

Specimen geometry was modified to allow higher stress application. Figure 44 shows insignificant corrosion on mild steel under stresses up to 16,300 psi in, as-received, weak liquor. The same results are apparent in the same liquor containing chloride (Fig. 45). Preliminary tests in white liquor show similar results (Fig. 46). Very high corrosion rates occur with stressed steel early in exposure until corrosion products become stable and the rate of corrosion drops significantly. This implies that removal of products after stability will revert the corrosion to high levels. Verification is required, since it leads to consideration of the

danger of impact, abrasion, and, perhaps, cleaning with mill processes in stressed vessels. Further work is also required to eliminate technique problems and to study higher stress levels.

TABLE X

CORROSION RATE OF MILD STEEL IN AS-RECEIVED, WEAK BLACK LIQUOR (FIRST BSW[a] 90°C)

Applied Stress (psi)	Linear Polarization (mpy)
0	1
1000	3
2000	3
3000	3

[a]BSW - Brown Stock Washing.

Accelerated Tests - Electrochemical

Several test campaigns have been conducted to accelerate the corrosion of the test metals in weak liquors. Table XII shows the corrosion rates of both metals exposed to weak liquor for one hour under the application of +800 mv, S.C.E., "zap" potential. Please note these are weight loss measurements on mild steel in as-received, weak black liquor. Note also that stainless steel is corroded by this technique! These results, as well as the appearance of the samples, indicate lower potentials can be used to produce measurable corrosion. The data also indicate a need for improved reproducibility. Figure 47 shows how the migration of liquor solids leads to accumulation on the specimen surface during zap tests. X-ray diffraction of these solids indicated amorphous material with a high background of iron. Since these solids as well as sludge-type deposits found in weak liquor storage tanks were identified with severe corrosion, further duplication and analyses are warranted. Subsequent applied potential tests indicate that significant and

reproducible corrosion rates on mild steel can be obtained at potentials of +450 mv for 3 hours.

TABLE XI

CORROSION RATE OF MILD STEEL IN WEAK BLACK LIQUOR
2000 psi, (4000 ppm NaCl), 90°C

Test No.	Weight Loss (mpy)	Linear Polarization Final Reading (mpy)
1	5.3	13
2	12.7	16
3	6.8	18
4	7.5	13

TABLE XII

CORROSION RATE OF MILD STEEL AND 304 STAINLESS STEEL IN WEAK BLACK LIQUOR
150°F, +800 mv (S.C.E.) APPLIED POTENTIAL FOR 1-HR

Specimen	Weight Loss (mpy)
Mild steel	726
Mild steel	764
Mild steel	660
304	9.6
304	6.7
304	8.8

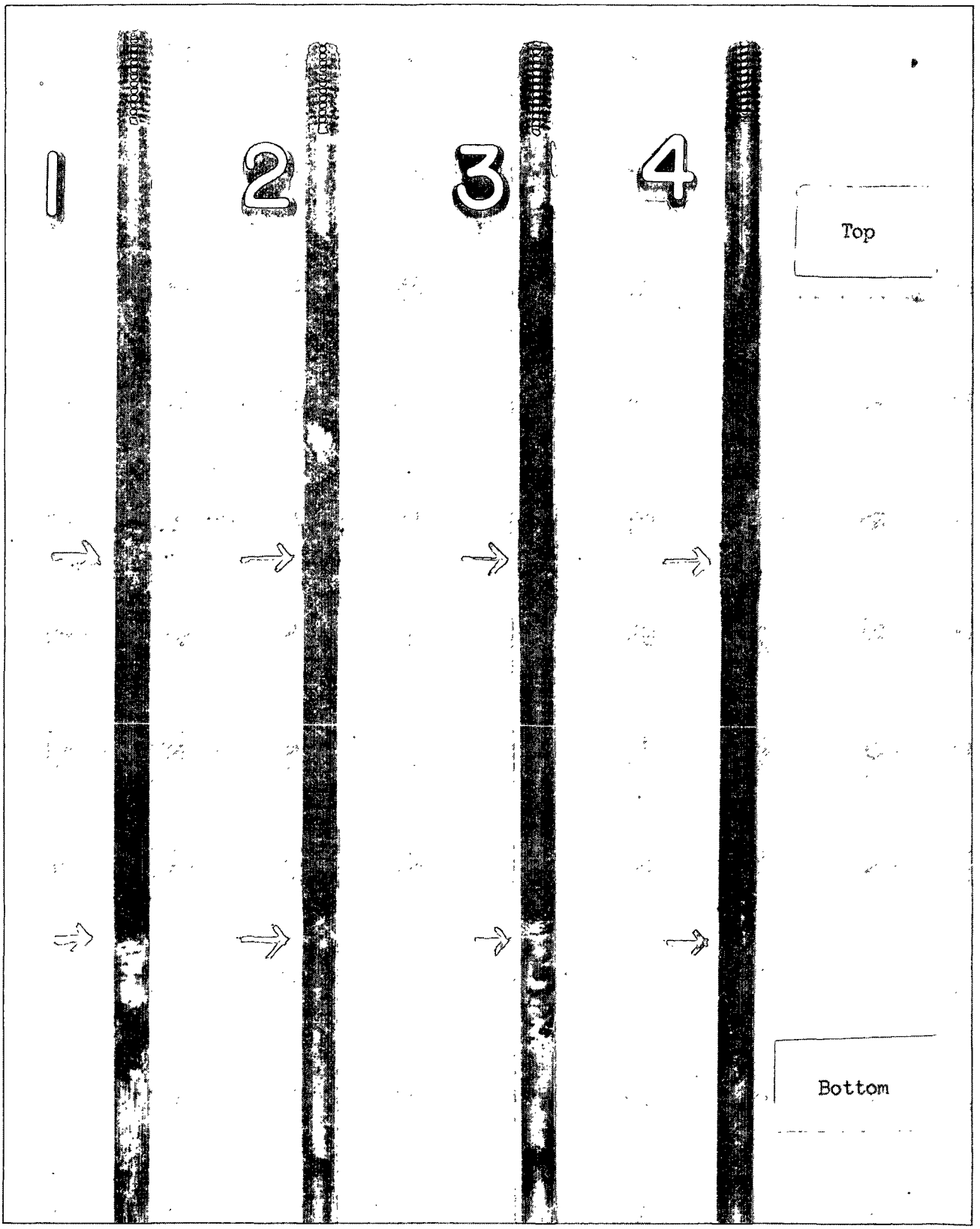

Figure 42. Stress-related corrosion, 1/4-inch rods in weak liquor, 2000 psi, 4000 ppm Cl, after test.

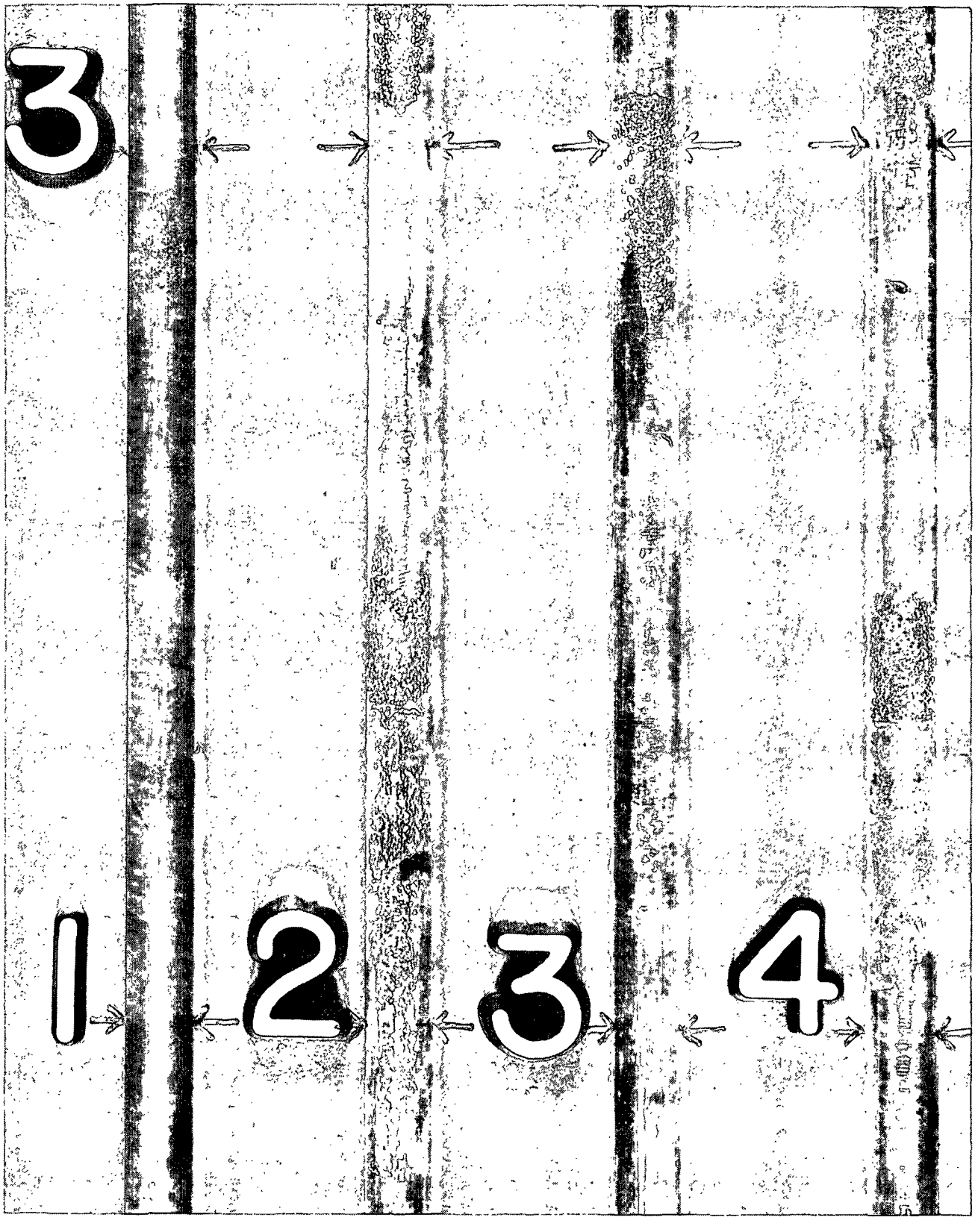

Figure 43. Stress-related corrosion, 1/4-inch rods in weak liquor, 2000 psi, 4000 ppm Cl, after cleaning.

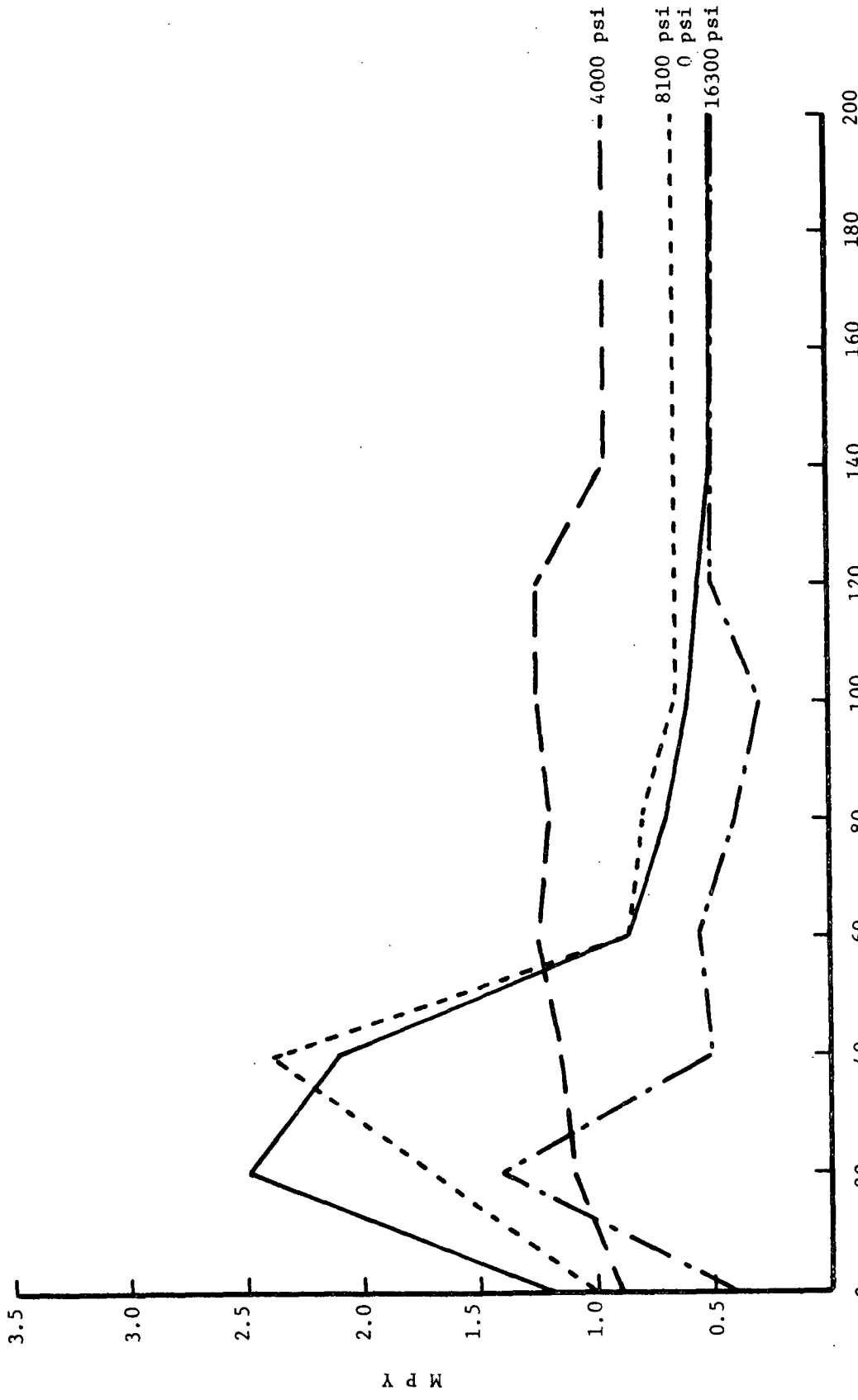

Figure 44. Corrosion rate of mild steel under the indicated levels of stress in weak black liquor, 90°C, pH 12.5.

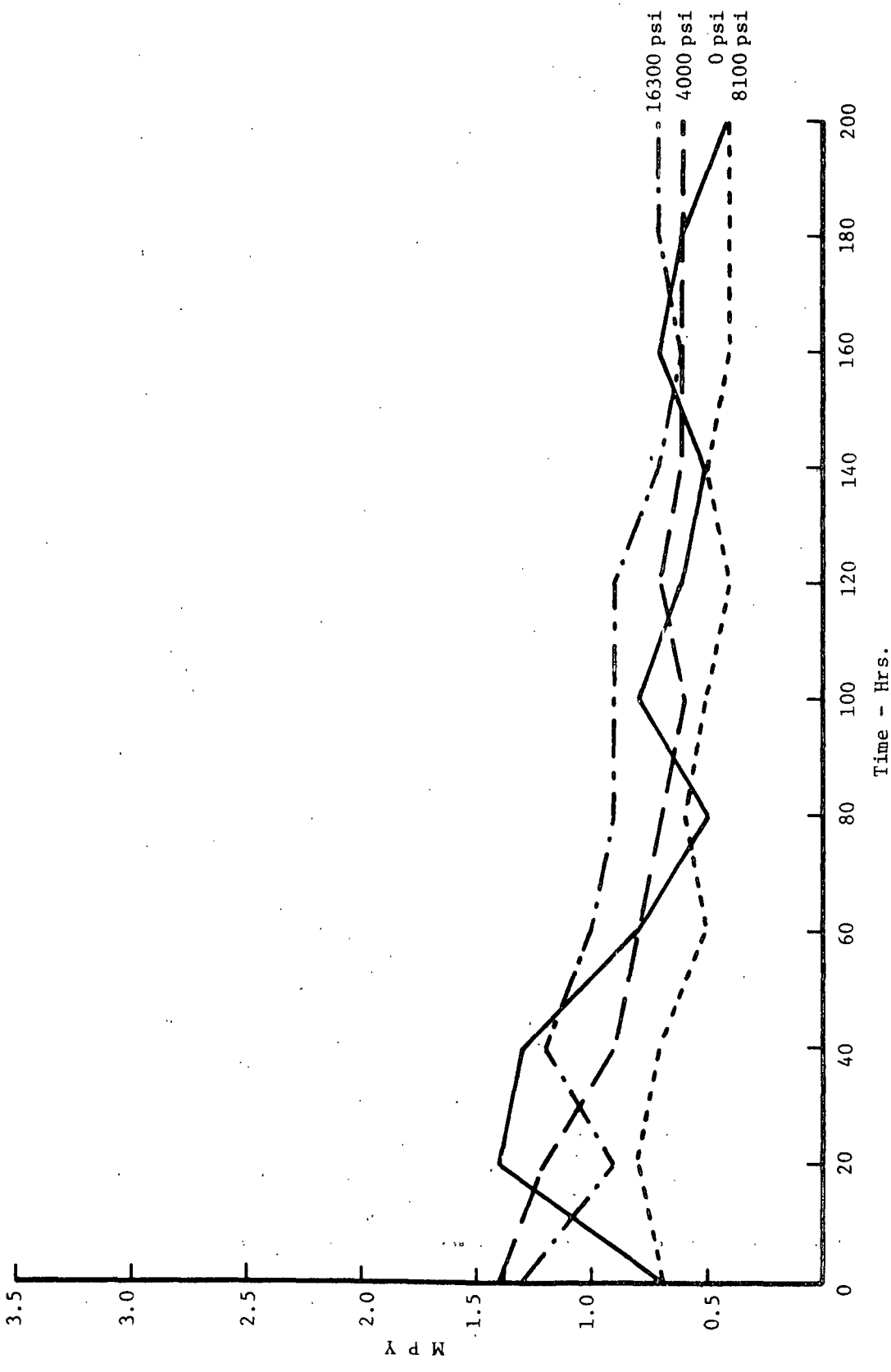

Figure 45. Corrosion rate of mild steel under stress, as indicated, in weak liquor containing 4000 ppm chloride, 90°C, pH 12.6.

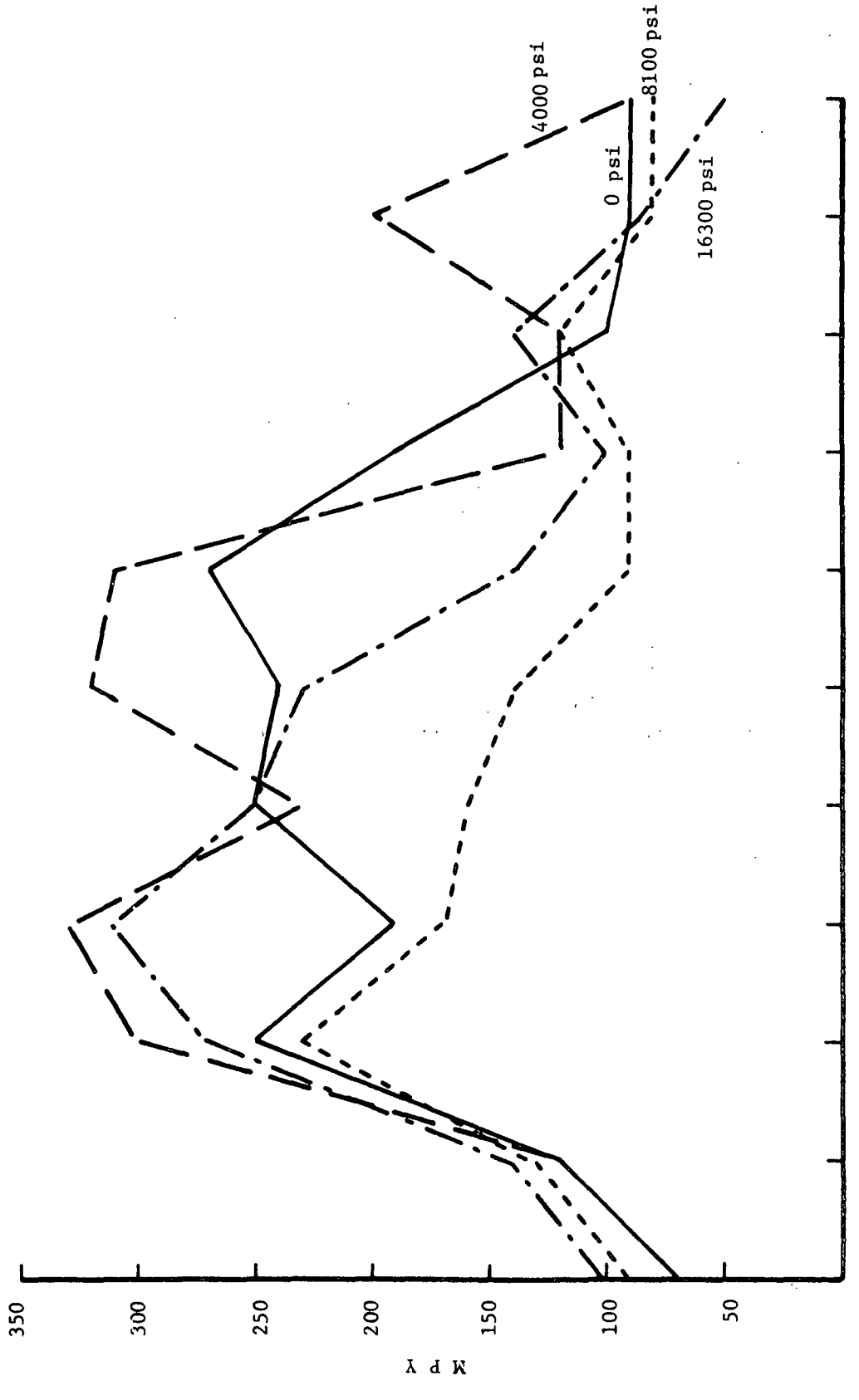

Figure 46. Corrosion rate of mild steel in white liquor under stress, as indicated, 90°C, pH 13.5.

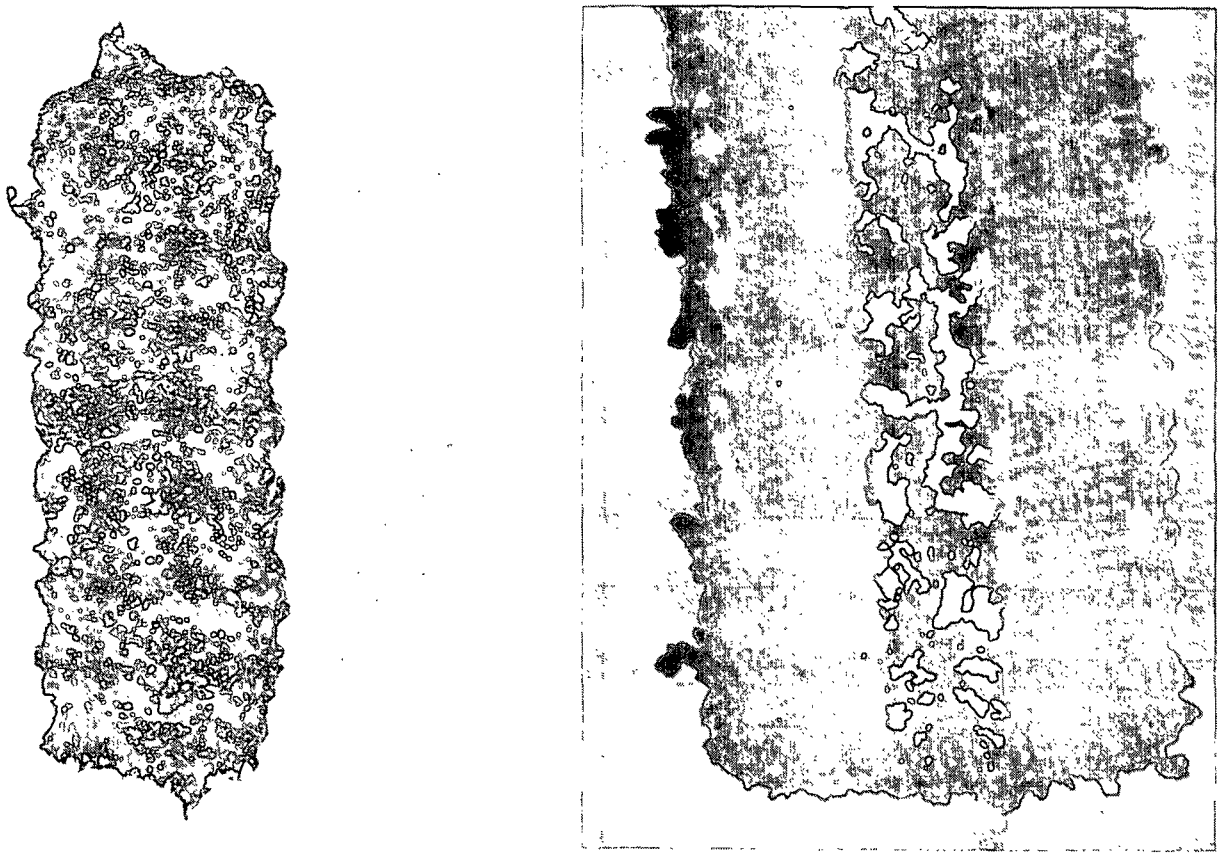

Figure 47. Solids formation on steel electrode in "zap" test at 800 mv. Solids analyzed as amorphous material containing large amounts of iron.

A LITERATURE REVIEW OF CORROSION STUDIES IN KRAFT LIQUOR AND/OR RELATED ENVIRONMENTS

Gouda et al. studied the effect of stress on the corrosion of steel in a simulated cement environment (1). The test environment contained 10^{-3} to 10^{-1} mol of NaCl, K_2SO_4, and Na_2S in saturated lime water. Electrochemical corrosion behavior was described for specimens under no-load and one-half yield stress. Changes in potential under open-circuit and applied (anodic polarization) potential tests were related to corrosion product film formation. Small pores and/or ruptures in the film were assumed anodic areas which increase in bare surface areas under stress. Heavy pitting was observed on no-load and stressed specimens by increasing the chloride (from 10^{-2} to 10^{-1}N Cl ion) in lime water. Similarly, increased sulfate and sulfide concentrations caused unstable film conditions as observed by potential readings. Corrosion rate measurements were not reported in this study.

Wensley and Charlton conducted potentiostatic polarization tests on mild steel in caustic/sulfur solutions similar to white liquor (2). The results show that increased caustic (from 20 to 200 gpl*) or temperature (from 25 to 90°C) in purely caustic solutions increase the primary passive current, i.e., more active oxidation kinetics prior to achieving passivity. The addition of thiosulfate to caustic solutions also enhanced the current maximum, thus defined as a corrosion activator. Although activation at thiosulfate levels of 0.5, 3.2, and 33.2 gpl were demonstrated by polarization curves, the effect was reported for levels as low as 0.1 gpl. Similarly, sulfide was identified as a corrosion activator over the range of 2 to 33 gpl added to caustic. Sodium sulfite and sulfate additions show no significant effect on polarization.

*gpl = grams per liter.

In a later study, the same authors report results of extensive weight-loss (coupon) testing of mild steel in white liquor clarifier environments (3). The study evaluated the corrosion resistance of a wide variety of mild steel compositions. In addition, it identified galvanic acceleration of mild steel coupled to stainless steel (20:1, area ratio) in white liquor of high corrosivity and, in contrast, protection in liquors of low corrosivity. It also showed the cracking of mild steel coupons occurred at stamped identification markings, particularly thinner coupons which would contain higher residual stresses. The latter effect was particularly true for liquors with high sulfide, low caustic levels. On the basis of this evaluation, an ASTM A285C with $<0.02\%$ silicon and $\geq 0.2\%$ copper was recommended for white liquor equipment.

Further investigations of caustic, caustic/sulfide environments were reported by anodic polarization test results for mild steel (4). This work not only confirmed previous results of the role of sulfide in deterring passivity of mild steel exposed to caustic, but it showed (by analysis of surface films) that S^{2-} ions penetrated the Fe_3O_4 film, thereby causing a loss of protection. In separate studies, the same author and others showed that carbon steel undergoes stress corrosion cracking in white liquor (5). Slow strain rate, applied potential tests showed the brittle, stress corrosion fracture mode was maximum in the active-passive transition potential.

Finally, a very intensive study of the corrosion resistance of various stainless steels in digester liquors has been reported (6). It shows that ferritic alloys and/or low nickel, austenitic ferritic alloys are better than the conventional austenitic steel as cladding in batch digesters.

FUTURE WORK

There are very few major changes in the research plan, previously submitted for 1982. This plan was prepared on the basis of Phase II results, after review with FKBG, and always in view of work reported by others. The major objective of future work is still the same, i.e., to define the limitations of mild steel as a construction material and to pinpoint alternate, cost-effective, protective measures when these limitations are exceeded. From the standpoint of corrosion testing, Phase II attests to the fact that this is easier said than done. It requires accurate, reproducible tests, and analyses which we have only just begun for kraft liquor systems. Liquor chemistry will continue to change, and it is important to have a capability to evaluate corrosivity affected by those changes. In this regard, one major change in the research plan would be to study the effect of thiosulfate on weak and heavy black liquor corrosivity rather than the originally planned carbonate additions.

In the recent past, there has been considerable concern that corrosion tests in the lab fail to simulate corrosion-related failures in the field. Aside from the uniqueness of individual mill processing, corrosion failures in this work were reported, not inspected. Therefore, future emphasis should be placed on direct, on-site inspection of failures. However, the need to correlate corrosion damage to measurements with conventional test apparatus is also apparent, as proposed.

In view of recent emphasis on white liquor corrosivity, this aspect of the overall study could be dropped with one exception and/or suggestion. Rather than resolving mild steel corrosion by constructing an all stainless steel pulp mill (and still further work is appropriate to evaluate this "fix"), investigation of the use

of nonmetals is suggested, e.g., liners for storage, perhaps clarification tooks (evaluation or proposed). Finally, the future plan calls for another survey and visitation program and, in this period of reflection, this could be particularly appropriate.

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